GROUP VI DERIVATIVES OF TERTIARY PHOSPHINES AND ARSINES

A thesis submitted to the
University of Glasgow in fulfilment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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ACKNOWLEDGEMENTS

I would like to express my sincere thanks to my supervisor, Dr. R.J. Cross, for his encouragement, advice and help, both in the preparation of this thesis and in its submission.

In addition, I would like to thank Dr. D.D. MacNicol and Dr. R. Keat for their assistance with certain aspects of this work.

ABSTRACT

Some radical reactions between certain tertiary phosphines and organic derivatives of sulphur, selenium and tellurium were investigated. The product mixture arising from the photochemically-initiated chain reaction between a 2:1 mixture of $Ph_2PCH{=}CH_2$ and HSC_3H_6SH, consisting mostly of $Ph_2P(S)C_2H_4SC_3H_7$ rather than the expected product $Ph_2PC_2H_4SC_3H_6SC_2H_4PPh_2$, was accounted for by the occurrence of thiyl radical ($RS^{\bullet}$) attack at P(III) to form an intermediate phosphoranyl radical (which decomposed to give the P(V) sulphide and a carbon-centred radical) as well as the desired free-radical addition of $RS^{\bullet}$ to the double-bond. The major product, $Ph_2P(S)C_2H_4SC_3H_7$, was thought to arise from a sterically favourable intramolecular ring closure from the $S^{\bullet}$ of $Ph_2PC_2H_4SC_3H_6S^{\bullet}$, because of the close proximity of $S^{\bullet}$ to its own P(III). Analogous photochemical reactions of some thiols with a phosphine and an olefin indicated that certain thiols react preferentially with an olefin whereas others favoured attack at the P(III) of the phosphine. The relative ease of elimination of the carbon-centred radical $R^{\bullet}$ from the intermediate phosphoranyl radical, $\left[R^1_3\overset{\bullet}{P}\text{-}S\text{-}R\right]$, (formed by the attack of $RS^{\bullet}$ at the phosphine) was considered to be the controlling feature of the reaction, and lent support to previous work where the reversibility of formation of thiophosphoranyl radicals in the reaction of RSH with $Ph_2PCH{=}CH_2$ was considered to be an important step leading to the formation of the observed products. The most important decomposition route for the phosphoranyl radical intermediate $Ph_2\overset{\bullet}{P}(SR)R^1$ was found to be (C-S) β-scission when $R^{\bullet}$ was an easily formed radical, but when $R^{\bullet}$ was less readily formed and $R^1{=}(CH_2)_nP(X)Ph_2$ (n=1,2;X=: or S) C-P scission became important, although (C-S) β-scission always occurred to an appreciable extent in each case. Tertiary phosphines, R^1_3P, were found to react with organic diselenides, R_2Se_2, under u.v. irradiation to produce R^1_3PSe and R_2Se. The reaction rates decreased in the orders $R^1_3 = Me_2Ph > MePh_2 > Ph_3$ and $R = PhCH_2 >$

Et > Me > Ph , consistent with the operation of a radical chain mechanism involving the radicals RSe$^{\bullet}$ and $R^1_3P^{\bullet}(SeR)$ as chain carriers. Although cleavage of Se-C bonds is known to be important in the u.v. irradiation of R_2Se_2 alone, Se-Se cleavage seemed to be the more important initiation step in the presence of tertiary phosphines. The variation in reaction rates for the different organic groups, R, was consistent with increasing energy of radical formation, indicating that the rate determining step might be the elimination of R$^{\bullet}$ from the phosphoranyl radical intermediate, $R^1_3P^{\bullet}(SeR)$. The α-scission of this selenophosphoranyl radical was found to occur, to a limited extent, only in those reactions where β-scission was relatively slow, or where the strength of the usually strong P-C bond in the tertiary phosphines, $Ph_2P(SeR)R^1$ (R^1= Ph,Me), was reduced, when R=CH_2PPh_2, to a point where P-C cleavage was as facile as C-Se cleavage. Ultraviolet irradiation of solutions of R_2Te_2 produced R_2Te and Te quantitatively. In the presence of tertiary phosphines, R^1_3P, the reactions were accelerated <u>via</u> the formation of R^1_3PTe which decomposed to liberate Te and reform R^1_3P. All the reactions could be satisfactorily interpreted in terms of an initiation step involving photochemical cleavage of Te-C bonds. The ease of cleavage of element-carbon bonds by u.v. irradiation therefore increases in the series R_2S_2 < R_2Se_2 < R_2Te_2, whereas the ease of cleavage of element-element bonds is the reverse.

Some synthetic routes to tertiary arsine sulphides were studied. The reaction of the tertiary arsines, R_3As, (R=Ph,Me,CH_2AsPh_2, and $C_2H_4AsPh_2$) with elemental sulphur gave good yields of R_3AsS only when heated at <u>ca.</u> 150 °C for a number of hours. $Ph_2As(S)CH_2As(S)Ph_2$ was not prepared due to the low reactivity of the As (III) in the initially formed $Ph_2As(S)CH_2AsPh_2$. Attempts to prepare some tertiary arsine sulphides by the reaction of the arsine with S_2Cl_2 at room temperature all failed, the tertiary arsine dichlorides being formed exclusively. An attempt was made

to prepare and isolate Ph_2MeAsS by bubbling H_2S through an ethanolic solution of $Ph_2MeAsCl_2$ (prepared from the arsine and S_2Cl_2). The product, however, was a colourless viscous liquid which was thermally decomposed to the arsine and sulphur under the conditions of the vacuum distillation used to try to obtain a pure sample of Ph_2MeAsS. This particular arsine sulphide also eluded isolation in a pure state when formed by the exchange of sulphur between Ph_3AsS and Ph_2MeAs. A crystalline adduct (1:1) of Ph_2MeAsS and $(Me_2N)_3PO$ (HMPA) was, however, isolable when the reaction of the arsine and sulphur was carried out in a benzene/HMPA solvent mixture. The discovery of this adduct prompted an investigation into factors affecting the formation of such adducts between Group VI derivatives of tertiary phosphines and arsines, R_3MX (M=P,As;X=O,S,Se). No other adducts were isolated, however, and it appeared to be quite difficult to rationalize the probability of adduct formation between such derivatives because it was not clear which adduct component behaved as the electron donor and which the electron acceptor in a particular case. Nevertheless, a rationale for the determination of the relative potential of such molecules to behave either as donors or acceptors was suggested and involved the relationship between the i.r. stretching frequency of the M-X bond and the bond's polarity. The smaller the frequency within a particular series of Group VI derivatives, the more polar was the M-X bond, resulting in an increased electron density at the X atom, enhancing the molecule's donor properties.

The exchange of selenium between tertiary phosphine selenides, R_3PSe, and the analogous tertiary phosphine, R_3P, was found to be fast on the n.m.r. time scale at elevated temperatures and to resemble more closely the analogous process with phosphine tellurides rather than that with phosphine sulphides. Thus, characteristic n.m.r. resonances of mixtures of R_3PSe and R_3P broadened and coalesced as the temperature was increased.

The coalescence points covered a wide range of temperatures making the determination of the exact coalescence temperatures difficult to measure accurately, but they were all obviously concentration dependent. This was consistent with intermolecular transfer of selenium. The coalescence temperatures of Ph_2MePSe with Ph_2MeP and $Ph_2P(Se)CH_2PPh_2$ with $Ph_2PCH_2PPh_2$ were comparable (ca. 140-165 °C, depending on the components' concentrations) whereas $Ph_2PC_2H_4PPh_2$ with its mono- and di-selenide coalesced at lower temperatures (ca. 95 °C). The nature of the substituents on phosphorus obviously affected the rate of selenium exchange. The exchange of tellurium between Ph_2MePTe and Ph_2MeP was fast on the n.m.r. time scale at ambient temperatures (35 °C). No separate ^1H n.m.r. signals for Ph_2MePTe were observed, but a single methyl doublet with a chemical shift downfield of Ph_2MeP itself and with a reduced coupling constant was observed. Variable temperature n.m.r. measurements revealed that the equilibrium between Ph_2MePTe and Ph_2MeP was temperature dependent, but the irreproduceability of the v.t. effects suggested that the exchange might involve free tellurium atoms rather than intermolecular tellurium transfer (not involving free Te), since these atoms could recombine with Ph_2MeP to form Ph_2MePTe, or precipitate as elemental tellurium (accounting for the irreproduceability). N.m.r. investigations showed that equimolar solutions of $Ph_2P(Se)CH_2P(Se)Ph_2$ and $Ph_2PCH_2PPh_2$ react quantitatively to produce $Ph_2P(Se)CH_2PPh_2$ immediately on mixing, whereas $Ph_2P(Se)C_2H_4P(Se)Ph_2$ and $Ph_2PC_2H_4PPh_2$ equilibrated to a 1:2:1 mixture of $Ph_2P(Se)C_2H_4P(Se)Ph_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ at a similar rate. The analogous reactions of phosphine sulphides were similar, although much slower. Equilibrium was reached after about 24 h at 160 °C, but required more than 40 days at 80 °C. The rate of chalcogen atom transfer between phosphines is thus seen to increase in the order $S \ll Se < Te$.

1,2-Bis(diphenylphosphinoselenoyl)ethane, $Ph_2P(Se)C_2H_4P$-

$(Se)Ph_2$, was found to form stable inclusion compounds when crystallised from various pure solvents. The tenacity with which the included molecules were held in the crystal lattice of this host varied from guest to guest. Thus, toluene, for example, was driven out of the host by heating the crystalline adduct under vacuum at 70 °C, whereas p-dibromobenzene was liberated only after heating at 170 °C. Of particular interest with regard to a potential commercial application, was the remarkable guest selectivity found when $Ph_2P(Se)C_2H_4P(Se)Ph_2$ was crystallised from certain solvent mixtures. Recrystallisation of the unsolvated host from an equimolar mixture of the xylene isomers and ethylbenzene led to the recovery of host material containing 97.5% p-xylene. The use of a co-solvent to increase the solubility of the host enabled removal of 33% of the p-xylene from such a mixture at a single crystallisation. Moreover, a similarly high selectivity for the para-isomer was retained for solvent mixtures of these components containing as little as 4% of that isomer. The preference shown by this host for p-xylene appeared to be general for p-disubstituted mononuclear aromatics of similar size. Thus, recrystallisation of the host from equimolar mixtures of the chlorotoluene isomers produced an adduct containing 98.3% p-chlorotoluene, and when crystallised from a mixture of the dichlorobenzene isomers led to an inclusion compound containing 94.8% of p-dichlorobenzene. The host-guest ratio for the adducts containing these para-isomers was nearly always ca. 3:1, whereas adducts with other guests showed a more variable ratio. Other molecules, structurally related to $Ph_2P(Se)C_2H_4P(Se)Ph_2$, also exhibited significant inclusion behaviour. Thus, $Ph_2P(Se)C_3H_6P(Se)Ph_2$ and $Ph_2P(S)C_3H_6P(S)Ph_2$ formed inclusion compounds (1:1 or 2:1 host-guest ratio) when crystallised from certain pure solvents. $Ph_2P(S)C_3H_6P(S)Ph_2$ alone exhibited some selectivity when recrystallised from an equimolar mixture of the xylenes and ethylbenzene, an adduct containing 58% p-xylene being isolated. This host,

in contrast to $Ph_2P(Se)C_2H_4P(Se)Ph_2$, formed an inclusion compound with *p*-diethylbenzene and confirmed that the size and shape of the potential guest molecule was critical in determining whether an inclusion compound could be formed or not. There was considerable scope for further research into the performance of this series of clathrate host compounds with regard to the separation of individual components of certain solvent mixtures.

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GENERAL INTRODUCTION

GENERAL INTRODUCTION.

Our knowledge of phosphorus compounds has expanded so rapidly in the last twenty years that it now constitutes a major branch of chemistry. Academic interest in phosphorus compounds has been matched by a steady growth of their commercial applications. The great majority of commercially used phosphorus compounds are inorganic. The fertilizer industry accounts for about 70% of the total phosphorus used, largely in the form of inorganic phosphates. Synthetic detergents, introduced about 1950, come second and animal foodstuffs third. The organic phosphorus compounds, commercially important since 1940, have numerous applications as pharmaceuticals, plasticizers, insecticides, etc., although they only utilise 2% of the total phosphorus manufactured. Organophosphorus insecticides, for example, are widely used in agriculture. Their use is likely to increase since they are fairly quickly decomposed in the soil and thus are less hazardous to wild life than the halogenated hydrocarbons.

Phosphorus, in some respects, rivals carbon in the structural diversity of its compounds. Like carbon, it occupies a central position in the periodic table and so can easily form bonds with both electronegative and electropositive elements. These bonds are generally strong and so, as with carbon, a wide range of phosphorus compounds exist.

The chemistry of phosphorus, the second element in Group V, resembles that of arsenic much more than that of nitrogen, the lightest element. Nitrogen is the most electronegative element in the group and is, like phosphorus, a non-metal. The most electropositive element, bismuth, on the other hand, is a typical metal. Arsenic and antimony are intermediate in character and are often called metalloidal.

A phosphorus atom, with an electron configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$, has three unpaired electrons in the outer 3p-orbitals which are available for chemical bonding. Phosphorus can be formally trivalent or pentavalent, using either three, or all five electrons in its outer shell to form shared electron pairs with other atoms. In the vast majority of its compounds, three, four or five covalent linkages are formed between the element and other atoms and among these, the four-coordinate compounds are both the most numerous and technically the most important.

One of the most controversial features of phosphorus chemistry in recent years has been the extent of participation of d-orbitals in the bonding of certain phosphorus compounds. A great deal of physical evidence for $d\pi$–bonding has been collected including various studies on the nature of the M-X bond in some Group VI derivatives of tertiary phosphines and arsines (M=P or As, and X=O,S, or Se)[1], important members of the four-coordinate class of compounds of these two Group V elements. It has been suggested that the M-X bond is a dative bond, $M\rightarrow X$, a double bond M=X, or a bond possessing a character intermediate between a single bond and a double bond, depending upon the extent of $p\pi-d\pi$ bonding between M and X.[1] Physical measurements such as dissociation energies of the M-X bond, infrared stretching frequencies of the M-X group, n.m.r. studies, and studies on the donor properties of the M-X group toward various Lewis acids indicate that the M-X bond is most accurately described by the last of the above three formulations. Whatever the nature of these bonds, it is quite clear that their high strength in R_3MX molecules confers great stability to such compounds. For instance, Me_3PO and Ph_3PO do not decompose below 700°C. The analagous phosphine sulphides, selenides, and tellurides, are thermally

less stable, presumably reflecting the lower dissociation energy of P=X (X=S,Se,Te) compared to P=O, and the corresponding lower bond orders in the S, Se, and Te compounds.

Tertiary phosphine chalcogenides of this type (R_3PX; R=alkyl, aryl; X=S,Se, or Te) are featured in chapter one of this thesis which is concerned with some radical reactions of tertiary and ditertiary phosphines, involving the formation of an intermediate phosphoranyl radical $R_3\dot{P}XR^1$ (R,R^1=alkyl, aryl; X=S,Se, or Te). These radicals decompose by various routes, but frequently lead to the formation of R_3PX as a major product.

Chapter two describes our attempts to synthesize some analogous tertiary arsine sulphides, which led to a study on the ability of such compounds to form stable 1:1 adducts with certain other tertiary phosphine chalcogenides.

The nature of some chalcogen atom exchange reactions between tertiary phosphine chalcogenides and their equivalent tertiary phosphines is investigated in chapter three, and finally chapter four describes the previously unexpected tendency of some ditertiary - phosphine and - arsine chalcogenides to form molecular inclusion compounds. The high selectivity shown by some of these molecules when recrystallised from certain solvent mixtures is remarkable, and may enable them to be used in the commercial separation of hydrocarbon mixtures.

CHAPTER 1

RADICAL REACTIONS OF ORGANOPHOSPHORUS (III) COMPOUNDS

INTRODUCTION

Radical Reactions of Organophosphorus (III) Compounds

In general, phosphorus compounds react by ionic routes, using the nucleophilic reactivity of the lone pair of electrons in tervalent compounds, or the electrophilicity of the phosphorus atom in quinquevalent compounds. Radical mechanisms, however, are also quite common, and seem likely to become a topic of increasing importance both chemically and biologically. For example, Parathion, a widely used insecticide, is relatively harmless to mammals until exposed to ultraviolet irradiation when it is converted, presumably by a photolytically induced free radical reaction, to a compound with increased mammalian toxicity.[2] Furthermore, it is important to understand the effect of high-energy radiation on phosphorus compounds, since X-rays and γ-rays are being increasingly used in food preservation.

For these, and many other reasons, there has been a steadily increasing interest in the chemistry of phosphorus radicals. There are, in fact, two distinct types of phosphorus radical. The first has seven electrons in the valence shell of the phosphorus atom and is known as a phosphinyl radical, $R_2P^{\bullet}$. Such radicals can be relatively stable, for example, $Ph_2P^{\bullet}$ has a half-life of twenty minutes at 173 K, and they react either by addition (1) or radical abstraction (2).

$$R_2P^{\bullet} + X{=}Y \longrightarrow R_2P\text{-}X\text{-}Y^{\bullet} \qquad (1)$$

$$R_2P^{\bullet} + X\text{-}Y \longrightarrow R_2PX + Y^{\bullet} \qquad (2)$$

The second radical type has nine electrons around phosphorus, and is known as a phosphoranyl radical, $R_4P^{\bullet}$. The presence of unoccupied low energy d-orbitals makes valence shell expansion of second (and higher) row elements possible. Thus P(III) compounds can react with a free

radical to increase the coordination number to four and give a species, having nine valence electrons, one of which, at least, must populate the 3d-orbital.

$$X^{\bullet} + PR_3 \rightleftharpoons \dot{X}PR_3$$

The formation of such a phosphoranyl radical[3] was first suggested in 1957. Loss of R$^{\bullet}$ from this intermediate phosphoranyl radical would result in the overall homolytic substitution of R for X (3).

$$\dot{X}PR_3 \longrightarrow XPR_2 + R^{\bullet} \qquad (3)$$

In addition to this **α**-scission pathway for the decomposition of $\dot{X}PR_3$, it may also undergo **β**-scission, mainly on account of the strength of the P=O and P=S bonds in P(V) compounds. For example, when di-t-butyl peroxide reacts with triethyl phosphite (either thermally with a radical initiator or photochemically) the products are triethyl phosphate and hydrocarbon mixtures arising from alkyl radical dimerization and disproportionation[4] (equations 4 and 5).

$$^{t}BuO^{\bullet} + P(OEt)_3 \longrightarrow {}^{t}BuO\dot{P}(OEt)_3 \qquad (4)$$

$$^{t}BuO\dot{P}(OEt)_3 \longrightarrow {}^{t}Bu^{\bullet} + O{=}P(OEt)_3 \qquad (5)$$

When di-t-butyl peroxide reacts with an excess of tri-n-butylphosphine, however, the products are t-butyl-di-n-butyl phosphinite and tri-n-butylphosphine oxide in the ratio 4:1[5].

$$^{t}BuO^{\bullet} + P(^{n}Bu)_3 \longrightarrow {}^{t}BuO\text{-}\dot{P}(^{n}Bu)_3$$

$$^{t}BuOP(^{n}Bu)_2 + {}^{n}Bu^{\bullet} \xleftarrow{\alpha\text{-scission}} \quad \big| \quad \xrightarrow{\beta\text{-scission}} O{=}P(^{n}Bu)_3 + {}^{t}Bu^{\bullet}$$

The combination of t-BuO$^{\bullet}$ radicals with tri-t-butyl-phosphite has been shown to be irreversible[6] since reaction of ^{14}C labelled t-BuO$^{\bullet}$ radicals with the phosphite gave phosphate containing 75% of the original label (no label being detected in the unreacted phosphite), as would

have been predicted from a statistical cleavage of the intermediate phosphoranyl radical (equation 6).

$$(^{t}BuO)_3P + {}^{t*}BuO^{\bullet} \longrightarrow (^{t}BuO)_3\dot{P}\text{-}O\text{-}{}^{t*}Bu \begin{cases} \nearrow (^{t}BuO)_3P{=}O + {}^{t*}Bu^{\bullet} \ (25\%) \\ \searrow (^{t}BuO)_2P(O)O{}^{t*}Bu + {}^{t}Bu^{\bullet} \ (75\%) \end{cases} \qquad (6)$$

* = ^{14}C label

Phosphoranyl radicals can also be generated by an alternative route involving the reaction of alkyl radicals with the phosphoryl group.[7] For example, t-butyl peroxy radicals react with triethyl phosphite to give t-butoxy radicals and triethyl phosphate (7). The t-butoxy radicals then decompose to give acetone and methyl radicals (8), and the latter attack triethyl phosphate at phosphoryl oxygen to produce a phosphoranyl radical and ultimately diethylmethyl phosphate (9).

$$^{t}BuOO^{\bullet} + (EtO)_3P \longrightarrow (EtO)_3P{=}O + {}^{t}BuO^{\bullet} \qquad (7)$$

$$^{t}BuO^{\bullet} \longrightarrow Me_2C{=}O + Me^{\bullet} \qquad (8)$$

$$Me^{\bullet} + (EtO)_3P{=}O \longrightarrow (EtO)_3\dot{P}\text{-}OMe \longrightarrow (EtO)_2P(O)OMe + Et^{\bullet} \qquad (9)$$

By analogy with the reaction of alkoxy radicals, alkylthiyl radicals would be expected to form phosphoranyl radicals by addition to P(III) compounds. In the course of an investigation of exchange reactions of trialkyl phosphites, Hoffman and co-workers[8] observed that the reaction of thiols took an unexpected course to yield hydrocarbon and phosphorothionate (10).

$$RSH + P(OEt)_3 \longrightarrow RH + S{=}P(OEt)_3 \qquad (10)$$

Reaction (10) was further studied by Walling and Rabinowitz,[4] who showed that an analogous process occurred with alkyl disulphides (11).

$$RSSR + P(OEt)_3 \longrightarrow RSR + S{=}P(OEt)_3 \qquad (11)$$

Both were proposed as radical chain processes initiated by heating in the

presence of typical radical initiators or by ultraviolet irradiation at room temperature.

To account for their results they suggested the propagation steps shown in equations (12) - (15).

$$RS^{\bullet} + P(OEt)_3 \longrightarrow RS\text{-}\dot{P}(OEt)_3 \quad (12)$$

$$R\text{-}S\dot{P}(OEt)_3 \longrightarrow R^{\bullet} + S{=}P(OEt)_3 \quad (13)$$

$$R^{\bullet} + RSH \longrightarrow RH + RS^{\bullet} \quad (14)$$

$$R^{\bullet} + RSSR \longrightarrow RSR + RS^{\bullet} \quad (15)$$

The facile hydrogen transfer (14) makes the thiol reaction a particularly long chain sequence. Radical displacement on the sulphur of a disulphide (15), however, is a slower process and therefore fewer chain cycles occur.

Walling, Basedow and Savas[9] have shown that thiyl radicals (generated from thiols) also attack tertiary phosphines. For example, n-butyl thiol and tri-n-butylphosphine react at 60°C in the presence of an initiator (16).

$$^{n}BuSH + (^{n}Bu)_3P \longrightarrow {}^{n}BuH(75\%) + (^{n}Bu)_3PS(93\%) \quad (16)$$

Reaction (12) has been demonstrated directly by the observation at -93°C of the e.s.r. spectra[10] of the $MeS\dot{P}(^{n}Bu)_3$ and $MeS\dot{P}(OEt)_3$ phosphoranyl radicals when an isopentane solution of dimethyl disulphide and the appropriate phosphine or phosphite was irradiated with u.v. light in the cavity of an e.s.r. spectrometer (17 ; R=^{n}Bu, EtO).

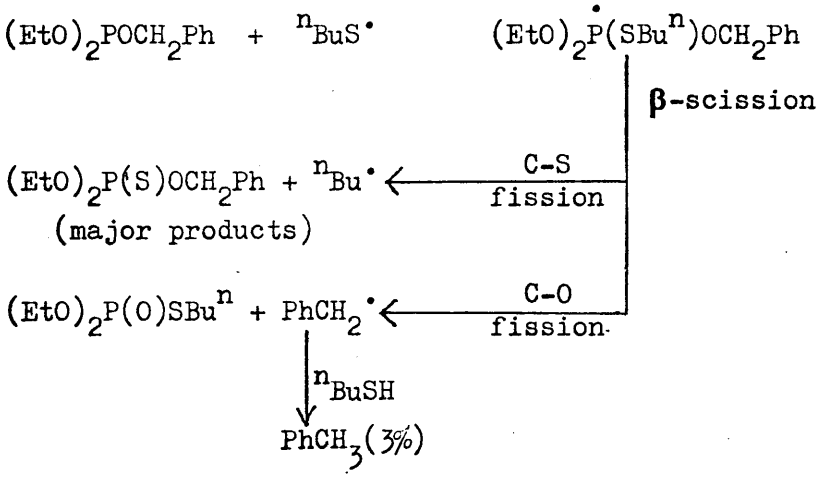
$$Me_2S_2 \xrightarrow{h\nu} 2MeS^{\bullet} \xrightarrow{PR_3} MeS\dot{P}R_3 \quad (17)$$

They were unable to detect any intermediate phosphoranyl radical when $^{t}Bu_2S_2$ was photolysed in the presence of trialkyl phosphines or phos-

phites. It was concluded that the lifetime of the undetected $^{t}BuSPR_3^{\bullet}$ radical must have been very short indeed, and that its formation and subsequent breakdown to give phosphine sulphide (or phosphorothionate) and the $^{t}Bu^{\bullet}$ radical was almost a concerted reaction and occurred very readily. Reaction (13) has also been shown to occur by the observation of the e.s.r. spectrum of the $^{t}Bu^{\bullet}$ radical when a solution containing di-t-butyl disulphide and tri-isopropylphosphine was irradiated with u.v. light[11] (18).

$$\underline{t}\text{-BuS}^{\bullet} + P(^{i}Pr)_3 \longrightarrow S{=}P(^{i}Pr)_3 + {}^{t}Bu^{\bullet} \qquad (18)$$

Walling and co-workers[9] investigated the possibility that β-scission involving the R-OP bond of the thiophosphoranyl radical may occur in favourable cases. The product from benzyl diethyl phosphite, which could in theory give the resonance-stabilised benzyl radical, and butane-1-thiol did in fact contain toluene (3%) as well as benzyl diethylphosphorothionate, indicating the occurrence of the following (19).



(19)

The selectivity in favour of the thiophosphoryl product is a reflection of the strength of the C-S bond (290kJ/mole) versus that of the C-O bond (360kJ/mole).

Decomposition of the phosphoranyl radical formed from $(EtO)_3P$ and PhSH[9], $(EtO)_3\dot{P}$-SPh, is remarkably slow, probably as a result of the small resonance energy of the resulting phenyl radical and the possibility of

additional strengthening of the Ph-S bond as a result of overlap between the π-electron system of the benzene ring and the unshared electron pairs of sulphur. Thus, irradiation for 10 h at 70°C resulted in the recovery of the starting materials, and only when the reactants were heated along with di-t-butyl peroxide at 145° did a slow reaction occur, allowing the isolation of 10-15% triethyl phosphorothionate and benzene from the products. The major products, which were demonstrated to be formed in the absence of peroxide in good yield, were found to be phenyl ethyl sulphide and diethyl phosphate, resulting from a competing ionic alkylation reaction (20).

$$\begin{array}{l} PhSH + (EtO)_3P \xrightarrow{\text{ionic}} PhSEt + OPH(OEt)_2 \ (85\%) \\ \qquad\qquad \xrightarrow{\text{radical}} PhH + SP(OEt)_3 \ (15\%) \end{array} \qquad (20)$$

Thiophenol was also found to strongly inhibit the reaction between butane-1-thiol and triethyl phosphite (reaction 10 ; R=^{n}Bu), indicating the preferential formation of benzenethiyl radicals.

Walling and Pearson[12] later capitalised on this difficulty with which the Ph-SP bond is broken to enhance the R-OP scission in (19) above. Replacing ^{n}BuSH by PhSH, toluene was indeed formed to a greater extent (10%) but so was benzene (4%). The major reaction again was probably heterolytic.

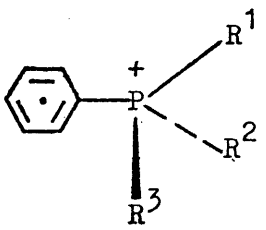
Oxyphosphoranyl radicals have also been observed using e.s.r. spectroscopy by Kochi and Krusic[11], who detected them in the reactions of ^{t}BuO$^{\bullet}$ radicals with phosphines (21 ; R=Me).

$$^{t}BuO^{\bullet} + PR_3 \longrightarrow R_3\dot{P}\text{-}O^{t}Bu \qquad (21)$$

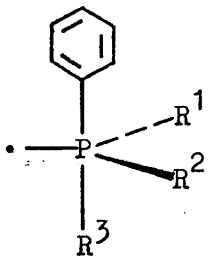
For R=Et, ^{i}Bu, ^{i}Pr, and c-C_6H_{11}, only the e.s.r. spectra of the displaced alkyl radicals, R$^{\bullet}$, were detected, indicating the short lifetime of these oxyphosphoranyl radicals and the relative ease with which α-scission

occurs in these reactions.

The structure of phenylphosphoranyl radicals, $PhP\dot{R}^1R^2R^3$, as deduced from their e.s.r. spectra, have been formulated[13] as those with essentially a tetrahedral arrangement of the ligands about phosphorus, the lone electron being located on the aromatic ring, (structure I), and those with an approximately trigonal bipyramidal structure with the unpaired electron acting as an equatorial 'phantom' ligand (structure II).



Structure I



Structure II

The e.s.r. spectra of trigonal bipyramidal phosphoranyl radicals have been found to exhibit large phosphorus hyperfine splittings[13] (usually 500-1000 Gauss) indicating that the unpaired electron occupied an orbital with appreciable (15-30%) phosphorus 3s-character, whereas the spectra of tetrahedral phenylphosphoranyl radicals had relatively low phosphorus hyperfine splittings (between 9 and 45 Gauss), and appreciable coupling to the aromatic protons indicated that the lone electron was located on the phenyl ring.

Davies, Parrott, and Roberts[13] studied a series of phenylphosphoranyl radicals in solution and noted that whereas the radical $Ph_2\dot{P}(O^tBu)OEt$ (formed by the attack of $^tBuO^\bullet$ on Ph_2POEt) should be classed as having tetrahedral geometry about phosphorus, $Ph_2\dot{P}(SMe)OEt$ (formed by attack of $MeS^\bullet$ on Ph_2POEt) should be classified as possessing trigonal bipyramidal geometry. Similarly, $Ph_3\dot{P}(O^tBu)$ was tetrahedral whereas

$Ph_3\dot{P}(SMe)$ was trigonal bipyramidal. The electronegativities of the groups R^1, R^2 and R^3 (structures I and II) were thought to control the amount of spin density in the phenyl ring, and thus the geometry of the radical. It was suggested that, as the ability of the groups R^1-R^3 to stabilize a positive charge on phosphorus increased, the greater was the likelihood that the electron density would reside on the aromatic ring, and hence, the introduction of electron-withdrawing groups would give rise to trigonal bipyramidal configurations with the odd electron strongly localised on the phosphorus atom, whereas a tetrahedral configuration would result when R^1-R^3 were electron-donating groups with the odd electron delocalised in the benzene ring. The phenyl group also apparently increased the rate of β-scission of these radicals by reducing the activation energy for this process[14].

Nishikida and Williams have suggested[15] that as greater spin density moves out from phosphorus to the apical ligands, so the lability of phosphoranyl radicals to α-scission should be increased. For example, $R_3\dot{P}O^tBu$ undergoes α-scission quite readily with the loss of an alkyl radical, R·[16](22 ; R=Me,Et).

$$^tBuO\cdot + PR_3 \longrightarrow R_3\dot{P}O^tBu \longrightarrow R_2PO^tBu + R\cdot \qquad (22)$$

For thiophosphoranyl radicals, $R_3\dot{P}SR^1$, α-scission has occurred only when R· was relatively stable ($R=PhCH_2$, ^tBu, Et_2P)[14], and since the phosphorus hyperfine splittings measured so far for such radicals have all been greater than 620 Gauss ($Ph_3\dot{P}SMe$ has the smallest recorded hyperfine splitting of 622.7 Gauss)[13], it may be that the lone electron resides wholly on the phosphorus atom, which coupled with the ease of cleavage of the C-S bond should cause the thiophosphoranyl radical to readily undergo β-scission.

The Generation of Organic Thiyl and Selenyl Radicals.

Alkyl- and aryl-thiyl radicals are known to be involved in the free-radical addition of thiols to olefins[17]. The photoinitiated reaction (23) is the common feature of all the examples.

$$RSH \xrightarrow{h\nu} RS^{\bullet} + H^{\bullet} \qquad (23)$$

Dialkyl disulphides have also been used extensively as sources of alkylthiyl radicals.

Windle and co-workers[18], studying the decomposition of diselenides, R_2Se_2, found that irradiation with 2537Å light at 77 K ruptured the Se-Se bond for $R=C_{12}H_{25}$ and $R=C_{18}H_{37}$ but not for $R=CH_3$, C_6H_5, or $C_6H_5CH_2$. Schmidt, Muller, and Markau[19], however, successfully photolysed diphenyl diselenide to give the trapped $PhSe^{\bullet}$ radical at 77 K. They also detected $PhTe^{\bullet}$ radicals using e.s.r. spectroscopy by the photolysis of diphenyl ditelluride in the gaseous state, followed by quenching of the radicals obtained at 77 K.

The reactions of organosulphur radicals are well authenticated and documented[20]. Authentic reactions of organoselenium radicals, in contrast, are hard to find in the chemical literature. The e.s.r. spectra of a small number of radicals containing selenium have been published, but, on the whole, very little is known about the generation and chemistry of such radicals.

The usual methods for making organosulphur radicals, for example, abstraction of a H atom from thiols and photolytic cleavage of disulphides, do not seem to have been applied to produce the analogous organoselenium radicals. The literature does contain examples of reactions of selenols and diselenides, but in no case has it been clearly shown that organoselenium radicals participate.

Petragnani and Schill [21] have found that diazomethane cleaves diphenyl or dibenzyl diselenides by a photochemical reaction to give selenoacetals in quantitative yield (24 ; R=Ph,$PhCH_2$).

$$R_2Se_2 + CH_2N_2 \xrightarrow{h\nu} RSeCH_2SeR + N_2 \qquad (24)$$

An analogous reaction occurred with the corresponding disulphides and ditellurides, the former in moderate yield (41%) and the latter quantitatively in the dark. A general mechanism involving a common intermediate, whether nucleophilic, carbene, or radical, could not, however, be confirmed. For example, with $:CCl_2$ (generated from $PhHgCCl_3$) replacing CH_2N_2 definite products could not be obtained[21]. The fact that the diselenide reaction with diazomethane was light-catalysed may support a radical mechanism (25-27 ; R=Ph,$PhCH_2$), although the two other mechanisms cannot be ruled out.

$$RSeSeR \rightleftharpoons 2RSe^{\bullet} \qquad (25)$$

$$RSe^{\bullet} + H_2C{=}\overset{+}{N}{=}\bar{N} \longrightarrow RSeCH_2\text{-}N{=}N^{\bullet} \longrightarrow RSeCH_2^{\bullet} + N_2 \qquad (26)$$

$$RSeCH_2^{\bullet} + RSe^{\bullet} \longrightarrow RSeCH_2SeR \qquad (27)$$

The photodecomposition of organic selenium and tellurium compounds has been known for over a century[22,23], and these photoreactions are quite often accompanied by formation of elemental selenium and tellurium. In spite of the interesting differences in photochemical behaviour of organochalcogen compounds, the literature contains very few structure-property relationships, and no detailed photochemical studies have been reported until quite recently.

In 1974, Stanley and co-workers[24], in a short communication, reported the first study on the solution-phase photochemical behaviour of organoselenium compounds. They found that irradiation (350 nm) of a benzene solution of dibenzyl diselenide in the absence of oxygen yielded

dibenzyl monoselenide and only a trace amount of elemental selenium along with other unidentified products (28).

$$(PhCH_2)_2Se_2 \xrightarrow{h\nu} (PhCH_2)_2Se + Se\ (trace) \qquad (28)$$

Chu, Marsh, and Gunther[25] repeated their experimental conditions and confirmed their stated results except that photodecomposition of the diselenide at 350 nm (and at 313 nm) resulted in the production of the monoselenide and a stoichiometric amount of red selenium. They found that when no ice-water cooling of the reaction vessel was employed only a trace of dark grey selenium was observed, and noted that the temperature in the reaction vessel reached 61°C after 40 minutes. The small yield of elemental selenium was considered to be consistent with thermally induced reactions leading to polymeric selenides as reported by Lardon[26]. They also found that the photodecomposition of dibenzyl diselenide was independent of initial concentration, but dependent upon absorbed light intensity and wavelength. At 365 nm only a small amount of photodecomposition could be detected after several hours irradiation. Their proposed mechanism for the photolysis of dibenzyl diselenide will be considered in the discussion section as it has a direct bearing on this work.

Cross and Millington[27] reported the photochemically-initiated reaction of diethyl diselenide with diphenylmethylphosphine, and suggested that a free-radical mechanism, similar to that with diorgano-disulphides and phosphines, operated involving the following sequence of reactions (29-32 ; R=Et).

$$R_2Se_2 \xrightarrow{h\nu} 2RSe^{\bullet} \qquad (29)$$

$$RSe^{\bullet} + Ph_2MeP \longrightarrow \left[Ph_2MePSeR\right]^{\bullet} \qquad (30)$$

$$[Ph_2MePSeR]^{\bullet} \longrightarrow Ph_2MePSe + R^{\bullet} \quad (31)$$

$$R^{\bullet} + R_2Se_2 \longrightarrow R_2Se + RSe^{\bullet} \quad (32)$$

The overall reaction produced quantitative yields of products (33 ; R=Et).

$$R_2Se_2 + Ph_2MeP \xrightarrow{h\nu} R_2Se + Ph_2MePSe \quad (33)$$

In contrast to the behaviour reported for a number of phosphines and phosphites, Harpp and Gleason[28] have found that disulphides are subject to facile desulphurisation by aminophosphines. Thus, although only acyl, thioacyl, and vinylogous acyl disulphides desulphurise with triphenylphosphine by an ionic mechanism involving nucleophilic attack of P(III) on the disulphide link, no reaction occurred with dibenzyl and diethyl disulphides under ionic reaction conditions[28]. On the other hand, tris(diethylamino)phosphine desulphurised dialkyl disulphides and some diaryl disulphides under mild conditions (34).

$$R_2S_2 + (Et_2N)_3P \longrightarrow R_2S + (Et_2N)_3PS \quad (34)$$

When R=$PhCH_2$, heating a benzene solution of the two reactants at 80°C for four hours resulted in the quantitative production of the phosphine sulphide and dibenzyl sulphide. When R=Et or ^{i}Pr, however, a reduced yield of products was obtained after heating at 80°C for 48 h, and when R=^{t}Bu the reaction only proceeded by 1% in 48 h[28].

Nuretdinov et al.,[29] have investigated the analogous reaction between tris(diethylamino)phosphine and dimethyl diselenide (35 ; R=Me).

$$R_2Se_2 + (Et_2N)_3P \longrightarrow R_2Se + (Et_2N)_3PSe \quad (35)$$

They heated a neat mixture of the reactants in a distilling flask at 120-140°C, the dimethyl selenide distilling out of the reaction mixture and forcing the reaction to go to completion. The mechanism was thought to be ionic although no attempt was made to determine whether or not the reaction was catalysed by free radicals, or inhibited by known radical inhibitors (e.g. hydroquinone).

In the absence of radical initiators or u.v.-irradiation the desulphurisation of disulphides and most likely the deselenation of diselenides by tertiary phosphines or phosphites are held to be ionic processes. Our study was concerned solely with u.v.-initiated reactions, therefore radical processes must predominate in every case, and the ionic mechanism may only become important when the radical route becomes disfavoured due to the formation of unreactive radicals.

RESULTS AND DISCUSSION

(a) Reaction of 1,3-propanedithiol with diphenylvinyl-phosphine.

From a study of the products of the u.v. light catalysed addition of thiols to diphenylvinylphosphine[30] it was apparent that the formation of the different products could be accounted for by RS$^{\bullet}$ radical attack on either phosphorus or olefin (scheme 1 ; R=C_6F_5,Ph,n-alkyl,^{i}Pr,^{t}Bu and CH_2Ph).

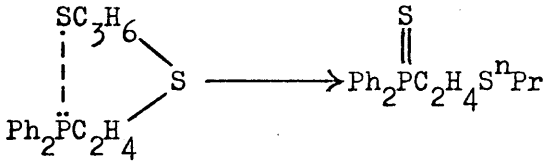
$$\begin{array}{ccc} RSH + Ph_2PCH{=}CH_2 & \longrightarrow & Ph_2PC_2H_4SR \\ \downarrow & & \downarrow RSH \\ Ph_2P(S)CH{=}CH_2 & \longrightarrow & Ph_2P(S)C_2H_4SR \end{array} \qquad \text{(scheme 1)}$$

The favoured route appeared not to depend on the nature of RS$^{\bullet}$, however, but on the ease of elimination of R$^{\bullet}$ from the intermediate phosphoranyl radical formed by attack of RS$^{\bullet}$ on P(III). If R$^{\bullet}$ was an easily formed radical like $PhCH_2^{\bullet}$ or $^{t}Bu^{\bullet}$, then formation of the phosphine sulphide resulted, whereas when R was n-alkyl or aryl, formation of $Ph_2PC_2H_4SR$ was preferred. This mechanism required either that RS$^{\bullet}$ attack on P(III) was readily reversible, or that the intermediate phosphoranyl radical, $Ph_2\dot{P}(SR)CH{=}CH_2$, readily rearranged intramolecularly to $Ph_2P\dot{C}HCH_2SR$.

In a continuation of this work we investigated the reaction between 1 mole of 1,3-propanedithiol and 2 moles of diphenylvinylphosphine (dvp), and although variable results were obtained, it was obvious that the product was a mixture of compounds, as indicated by ^{1}H and ^{31}P n.m.r. spectroscopy. The spectra showed that the major product was $Ph_2P(S)CH_2CH_2$-$SCH_2CH_2CH_3$, as the ^{1}H and ^{31}P n.m.r. spectra of an authentic sample of this compound (obtained by the reaction of an excess of n-propyl thiol with dvp[30]) were almost identical. The 1:1 reaction between this dithiol and dvp has been studied by Millington[31], who concluded that the sole product was $Ph_2P(S)C_2H_4S^{n}Pr$ (equation 36).

$$Ph_2PCH{=}CH_2 \;+\; HSC_3H_6SH \xrightarrow{h\nu} Ph_2P(S)C_2H_4S^nPr \qquad (36)$$

The product of the 2:1 phosphine-dithiol reaction was expected to be the potentially quadridentate ligand, $Ph_2PC_2H_4SC_3H_6SC_2H_4PPh_2$, formed by the radical addition of one molecule of dithiol to the double bonds of two vinylphosphine molecules. The competing thiyl radical addition to P(III), however, was obviously interfering with this reaction, and it was thought possible that the intermediate, $Ph_2PC_2H_4SC_3H_6SH$, (formed by the addition of one sulphur of the dithiol to the vinylphosphine) could not only react with another molecule of dvp (whether at P(III) or the double bond) but could also react intramolecularly to produce the major observed product (equation 37).



(37)

When the reaction (2:1) was carried out in a n.m.r. tube, the ^{31}P n.m.r. obtained after photolysis for 3 h showed that there were two P(III) compounds present, one of which was confirmed as unreacted dvp. The other was unidentified but it was noted that the signal appeared in the region typical of compounds with the general formula, $Ph_2PC_2H_4SR$ [30] (17 p.p.m. upfield from external H_3PO_4). There was no indication of any P(V) compounds, so this unidentified peak must have been either the intermediate $Ph_2PC_2H_4SC_3H_6SH$ or the expected product, $Ph_2PC_2H_4SC_3H_6SC_2H_4PPh_2$. Further irradiation must have led to the formation of $Ph_2P(S)C_2H_4S^nPr$. Meek and co-workers [32] also attempted this free-radical catalysed reaction between dvp and 1,3-propanedithiol (no indication of reactant ratio given), and they too obtained a mixture of compounds, concluding, as we have done, that β-scission had occurred to a large extent, rather than the desired free-radical addition to the double bond.

If we assume that the behaviour of $HSC_3H_6S^{\bullet}$ (or $Ph_2PC_2H_4SC_3H_6S^{\bullet}$) will be similar to that of $C_3H_7S^{\bullet}$, then the expected first product of the dithiol/dvp reaction would be $Ph_2PC_2H_4SC_3H_6SH$. The fact that no $Ph_2P(S)CH=CH_2$ was produced after photolysis of the n.m.r. tube mixture for 3 h supports this idea. The remaining SH group should similarly attack another molecule of dvp to produce $Ph_2PC_2H_4SC_3H_6SC_2H_4PPh_2$. The fact that $Ph_2P(S)C_2H_4S^nPr$ is formed preferentially, however, could be due to a favourable chelate-like ring closure from the S$^{\bullet}$ of $Ph_2PC_2H_4$-$SC_3H_6S^{\bullet}$, because of the close proximity of S$^{\bullet}$ to its own P(III) (equation 37) compared to any other phosphine molecule.

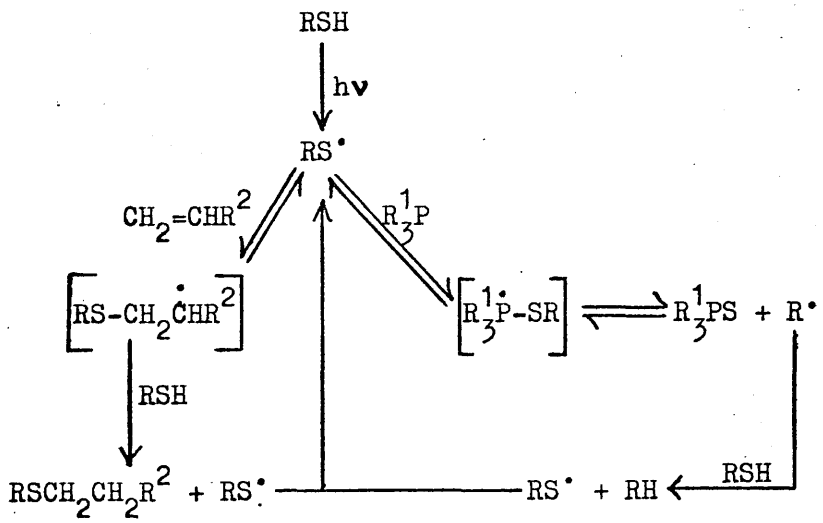
(b) The Reaction of Thiols or Disulphides with Phosphines and/or Olefins.

The radical reaction of thiols, RSH, with tertiary phosphines or phosphites produces P(V) sulphides [9,12], whereas with olefins, $CH_2=CHR^1$, thiols form diorganosulphides, $R^1CH_2CH_2SR$ [33].

The competition of thiyl radicals between triethyl phosphite and olefins has been examined previously[12]. The initial concentrations of the olefin (styrene or cyclohexene), n-BuSH, $(EtO)_3P$, and the final concentrations of the products, $(EtO)_3PS$ and the respective monosulphides, were all measured, and the results indicated that for styrene attack of RS$^{\bullet}$ at the double bond was more favoured than attack at P(III), whereas for cyclohexene RS$^{\bullet}$ attack at P(III) was preferred. Although the reversible nature of the addition of thiols to olefins was considered, no allowance was made for a reverse step operating on the addition to P(III) (although such a possibility was briefly mentioned later in the same paper.) Furthermore, only one thiol, n-BuSH, was used in that study. This is one of the cases to which we would assign a slow R$^{\bullet}$ elimination from an intermediate phosphoranyl radical, so that a reversible step here could markedly affect the product distribution. This could mean a much greater

rate of RS$^{\bullet}$ attack on P(III) than was reported.

It was felt desirable to find a mechanism which could account for the observation that certain thiols react preferentially with an olefin whereas other thiols favoured attack at P(III), when a phosphine/thiol/olefin mixture was irradiated with u.v. light. In the light of our observations on the reactions between thiols and diphenylvinylphosphine[30], the following scheme shows possible reaction routes (scheme 2).



SCHEME 2

If no step in the scheme was reversible then the reaction would be kinetically controlled and the most easily formed product would therefore be formed. If the various steps were all reversible (as shown in the scheme), however, then the reaction would be equilibrium controlled and the most stable product would predominate.

The photolysis of a neat mixture of thiophenol, PhSH, and α-methyl styrene, CH_2=CMePh, carried out in a n.m.r. tube under nitrogen, resulted

in complete reaction after 5 h irradiation, the anti-Markownikov addition product, $PhSCH_2CHMePh$, being formed almost exclusively. Similarly, the reaction between $PhCH_2SH$ and CH_2=CMePh was almost complete after 5 h irradiation, the anti-Markownikov product again having been formed.

When, however, a 1:1:1 mixture of PhSH, CH_2=CMePh, and diphenylmethyl-phosphine, Ph_2MeP, was irradiated for 18 h, the only product detected by ^1H n.m.r. spectroscopy was the unsymmetrical diorganomonosulphide, $PhSCH_2CHMePh$. The phosphine had apparently not reacted at all, as no signal due to the methyl protons of Ph_2MePS was detected.

When this same mixture was photolysed for 18 h, with $PhCH_2SH$ replacing PhSH, the major product was Ph_2MePS, formed by the attack of the thiol on Ph_2MeP, but some olefin addition product was also detected (accounting for about 25% of the product). The observation of significant amounts of toluene in this reaction also indicates that hydrogen abstraction from $PhCH_2SH$ by the benzyl radical is a much more facile process than the latter's addition to the olefin, and therefore it would appear that attempts to use the RSH/R_3^1P system as a $R^\bullet$ radical generator for addition to olefins are unlikely to be successful regardless of the nature of R.[30]

The energetics of the system were considered since it was thought likely that a particular thiol would not react exclusively with either the phosphine or olefin, but that a mixture of products would result. A ^1H n.m.r. study of the reaction between a series of thiols, RSH (R=Ph, ^tBu, $PhCH_2$), with α-methylstyrene (as a convenient olefin representative) and diphenylmethylphosphine (convenient because of its characteristic methyl protons), was undertaken to determine whether the percentage reaction with phosphine could be correlated with the "stability" of the $R^\bullet$ radical.

Firstly, benzene solutions of the three thiols with the phosphine were irradiated in a n.m.r. tube and it was observed that all of the thiols,

except thiophenol, reacted quantitatively according to equation (38) ($R=^{t}Bu, PhCH_2$)

$$RSH + Ph_2MeP \xrightarrow{h\nu} Ph_2MePS + RH \qquad (38)$$

Thiophenol apparently reacted only slightly producing a trace of Ph_2MePS along with other unidentified products; about 25% of the phosphine had not reacted. The thiols were also photolysed along with α-methylstyrene and it was confirmed that each produced the anti-Markownikov product, although it was noticed that $^{t}BuSH$ reacted very slowly. When the 1:1:1 mixtures were photolysed, it was observed that whereas PhSH had reacted exclusively with the olefin, $PhCH_2SH$ and $^{t}BuSH$ had both reacted approximately 75% with the phosphine, and 25% with the olefin although there was some doubt as to the exact nature of the products of the latter reaction, particularly in the $^{t}BuSH$ case, since it appeared that the $^{t}Bu^{\bullet}$ radical had reacted with the olefin as well as the $^{t}BuS^{\bullet}$ radical (a similar result occurred in the photolysis of diphenylvinyl-phosphine with $^{t}BuSH$[30]). This might also explain, to some extent, why very little olefin remained after approximately 17 h photolysis instead of the expected 75% unreacted olefin, although, more significantly, the photolysis of a benzene solution of $CH_2=CMePh$ alone resulted in about 40% decomposition of the olefin after 17 h.

Attempts were made to discover another suitable olefin less susceptible to photochemical decomposition, but a likely candidate, indene, proved to be even more susceptible to photochemical decomposition. It was therefore decided that the complexity of the reactions between the various thiols and phosphine/olefin mixtures precluded their further study, particularly by ^{1}H n.m.r. monitoring of the photolysis. Repetition of the above reactions on a larger scale (to enable product separation and identification) would most likely be advantageous, but it

was decided that the significance of the results obtained would not justify the efforts expended to attain them.

In conclusion, therefore, it is clear that benzyl thiol and t-butyl thiol react preferentially with the phosphine in a phosphine, thiol, olefin (1:1:1) mixture, whereas thiophenol reacts exclusively with the olefin. The results are consistent with the proposed mechanistic scheme (scheme 2), although they by no means prove that this mechanism operates as proposed. They also lend support to the proposed reversible formation of the intermediate phosphoranyl radical in the dvp/RSH reactions[30], since the relative ease of $R^{\bullet}$ elimination from the phosphoranyl radical in the phosphine-thiol-olefin system is consistent with that found in the dvp/RSH system. It has not proved possible to rule out conclusively the intramolecular rearrangement considered in the latter system, since no such rearrangement can occur in the former system. The results suggest, however, that the rearrangement does not occur to any significant extent.

In a study of the reaction of a series of alkylthiyl radicals, $RS^{\bullet}$ ($R={}^{i}Pr, {}^{t}Bu, p\text{-}MeC_6H_4CH_2$), with some diethyl alkylphosphonites, $R^1P(OEt)_2$ ($R^1=PhCH_2, {}^{t}Bu$), Bentrude and Rogers[34] concluded that an intermediate phosphoranyl radical, $R^1(RS)\dot{P}(OEt)_2$, was formed, which gave product via competitive α- or β-scission processes, the relative rates of which depended, to a first approximation, on the strengths of the C-P and C-S bonds undergoing scission. In an interpretation, which generally agrees with our early conclusions on the dvp/RSH system[30], they stated that only when $R^{1}\bullet$ was reasonably stable ($R^1={}^{t}Bu$, $PhCH_2$) did substitution by RS compete with oxidation, and that with less stable $R^{1}\bullet$, substitution might not be even thermodynamically a favourable process overall.

In contrast, other workers[35], in a study of the kinetics of the α-scission reactions of $R^1R^2\dot{P}(O^tBu)_2$ (R^1,R^2=alkyl) using e.s.r. spectroscopy, concluded that in none of the cases examined could the reactivity of the radicals be explained solely on the ease of C-P scission but that the relative stabilities of the trigonal bipyramidal permutational isomers of the phosphoranyl radicals were of primary importance.

We have studied the photochemically-initiated reaction of some thiols or disulphides with tertiary phosphines, following the progress of the reactions by ^{1}H n.m.r. spectroscopy. Mixtures (1:1) of the thiol or disulphide and the phosphine were dissolved in benzene in a n.m.r. tube and the extent of reaction monitored after various periods of irradiation. It became clear that although β-scission was the major pathway for the decomposition of the phosphoranyl radical, $Ph_2P(SR)R^1$(R=$PhCH_2$, Me; R^1=Me, $C_2H_4PPh_2$,CH_2PPh_2,$CH_2P(S)Ph_2$), other available decomposition modes also occurred to some extent, particularly with the ditertiary phosphines. The results of these reactions are presented in Table 1, along with a table listing the ^{1}H n.m.r. parameters of the major and minor products (Table 2).

The decomposition pathways available to the ditertiary phosphines used in this study are shown in schemes 3 and 4. The schemes were formulated to try to account for the observed products and should not be regarded as proof of the reaction routes actually occurring. In reaction 1 (Table 1) it should be noted that β-scission and ($P-CH_3$) α-scission of the intermediate phosphoranyl radical, $Ph_2\dot{P}(SMe)CH_3$, will both result in the formation of Ph_2MePS and Me_2S (the latter scission <u>via</u> the unstable S-methyldiphenylphosphinothioite, Ph_2PSMe, which, like other alkylphosphinothioites, should isomerise spontaneously under the conditions of the photolysis to the tertiary phosphine sulphide[36]). The

TABLE 1

Rxn. No.	Phosphine	Thiol/ Disulphide	Irrad^{n}, Time(h)	MAJOR PRODUCTS[a]	MINOR PRODUCTS[a]	POSSIBLE PRODUCTS[b]
1	Ph_2MeP	Me_2S_2	13	Ph_2MePS(44%); Ph_2MeP(41%)	Me_2S(10%)	$PhMe_2PO$(15%)[c]
			24	Ph_2MePS(74%)	Me_2S_2(46%); Me_2S(20%)	$PhMe_2PO$(19%)[c]
2	Ph_2MeP	$PhCH_2SH$	17	Ph_2MePS(90%); $PhCH_3$(80%)	$(PhCH_2)_2$(2%)	$Ph_2(PhCH_2)PS$(10%)
3	Ph_2MeP	-	4	Ph_2MeP(60%)		$PhMe_2PO$(12%)[c]
			24	Ph_2MeP(30%)		$PhMe_2PO$(15%)[c]; $PhMe_2P$(7%)
4	$Ph_2PCH_2PPh_2$	Me_2S_2	4	Ph_2MePS(31%); Ph_2MeP (26%); $Ph_2P(S)CH_2PPh_2$ (23%)	Me_2S(8%)	$PhMe_2PO$(13%)[c]
			18	Ph_2MePS(102%)	Ph_2MeP(15%); Me_2S(20%)	$PhMe_2PO$(25%)[c]
			42	Ph_2MePS(123%)	Me_2S(26%)	$PhMe_2PO$(30%)[c]

contd/.

TABLE 1 (Contd.)

Rxn. No.	Phosphine	Thiol/ Disulphide	Irrad$^{n.}$ Time(h)	MAJOR PRODUCTS[a]	MINOR PRODUCTS[a]	POSSIBLE PRODUCTS[b]
5	$Ph_2PCH_2PPh_2$	$PhCH_2SH$	4	$Ph_2P(S)CH_2PPh_2$(33%); $PhCH_3$(32%)	Ph_2MePS(7%); Ph_2MeP(4%)	
			12	$Ph_2P(S)CH_2PPh_2$(40%); $PhCH_3$(59%)	Ph_2MePS(19%)	$Ph_2(PhCH_2)PS$ (9%)
			66[d]	Ph_2MePS(43%); $PhCH_3$(87%)	$Ph_2P(S)CH_2P(S)Ph_2$(18%); $(PhCH_2)_2$(4%)	$Ph_2(PhCH_2)PS$ (24%)
6	$Ph_2PCH_2PPh_2$	$(PhCH_2)_2S_2$	4	$Ph_2PCH_2PPh_2$(76%)	$Ph_2P(S)CH_2PPh_2$(22%)	
			23	$Ph_2P(S)CH_2PPh_2$(65%); $(PhCH_2)_2$(41%)	Ph_2MePS(14%); $PhCH_3$(5%); $Ph_2P(S)CH_2P(S)Ph_2$(16%)	$Ph_2(PhCH_2)PS$ (19%)
			62	$Ph_2P(S)CH_2P(S)Ph_2$ (54%); $(PhCH_2)_2$(47%)	Ph_2MePS(20%); $PhCH_3$(18%)	$Ph_2(PhCH_2)PS$ (24%)

contd/.

TABLE 1 (Contd.)

Rxn. No.	Phosphine	Thiol/ Disulphide	Irrad$^{n.}$ Time(h)	MAJOR PRODUCTS[a]	MINOR PRODUCTS[a]	POSSIBLE PRODUCTS[b]
7	$Ph_2PCH_2PPh_2$	-	20	$Ph_2PCH_2PPh_2$(44%)	Ph_2MeP(10%)	Ph_2PPPh_2(?)
			68	$Ph_2PCH_2PPh_2$(25%)	Ph_2MeP(15%)	Ph_2PPPh_2(?)
8	$Ph_2P(S)CH_2PPh_2$	Me_2S_2	18	Ph_2MePS(32%);	$Ph_2P(S)CH_2P(S)Ph_2$ (18%)	$Ph_2(MeS)PS$(24%);
				$Ph_2P(S)CH_2PPh_2$(42%)		$Ph_2(MeSCH_2)PS$ (21%)
			60	Ph_2MePS(45%); $Ph_2P(S)CH_2P(S)Ph_2$ (27%)	$Ph_2P(S)CH_2PPh_2$(12%)	$Ph_2(MeS)PS$(36%) $Ph_2(MeSCH_2)PS$(21%)
9	$Ph_2P(S)CH_2PPh_2$	$PhCH_2SH$	4	$Ph_2P(S)CH_2P(S)Ph_2$ (38%); $PhCH_3$(36%)	Ph_2MePS(4%)	
			46	$Ph_2P(S)CH_2P(S)Ph_2$ (64%); $PhCH_3$(64%)	Ph_2MePS(24%)	$Ph_2(PhCH_2)PS$(12%)

contd/.

TABLE 1 (Contd.)

Rxn. No.	Phosphine	Thiol/ Disulphide	Irrad[n]. Time(h)	MAJOR PRODUCTS[a]	MINOR PRODUCTS[a]	POSSIBLE PRODUCTS[b]
10	$Ph_2P(S)CH_2PPh_2$	$(PhCH_2)_2S_2$	13	$Ph_2P(S)CH_2P(S)Ph_2$(68%); $(PhCH_2)_2$(18%)	$PhCH_3$(9%)	
			36	$Ph_2P(S)CH_2P(S)Ph_2$(95%); $(PhCH_2)_2$(23%)	$PhCH_3$(18%); Ph_2MePS(9%)	
11	$Ph_2P(S)CH_2PPh_2$	-	21	$Ph_2P(S)CH_2PPh_2$(90%)	Ph_2MePS, Ph_2MeP(traces)	
			46	$Ph_2P(S)CH_2PPh_2$(80%)	Ph_2MePS(6%); Ph_2MeP(2%)	
12	$Ph_2PC_2H_4PPh_2$	Me_2S_2	3[e]	Ph_2MePS(68%); Ph_2MeP(31%) $Ph_2P(S)C_2H_4P(S)Ph_2$(32%)	Me_2S(21%); $CH_2=CH_2$(21%)	$PhMe_2PO$(20%)[c]
			20	Ph_2MePS(90%); $Ph_2P(S)C_2H_4P(S)Ph_2$(28%)	Me_2S(22%); $CH_2=CH_2$(17%)	$PhMe_2PO$(23%)[c]
13	$Ph_2PC_2H_4PPh_2$	$PhCH_2SH$	6	$Ph_2PC_2H_4PPh_2$(64%)	$Ph_2P(S)C_2H_4PPh_2$(15%); $PhCH_3$(10%); $CH_2=CH_2$(9%)	
			43	$Ph_2P(S)C_2H_4PPh_2$(18%) $PhCH_3$(27%); $CH_2=CH_2$(20%)	$Ph_2P(S)C_2H_4P(S)Ph_2$(6%) $Ph_2PC_2H_4PPh_2$(16%)	$(PhCH_2)_2S$(11%)

contd/.

TABLE 1 (Contd.)

Rxn. No.	Phosphine	Thiol/ Disulphide	Irrad[n]. Time(h)	MAJOR PRODUCTS[a]	MINOR PRODUCTS[a]	POSSIBLE PRODUCTS[b]
14	$Ph_2PC_2H_4PPh_2$	-	6	$Ph_2PC_2H_4PPh_2$(74%)	$CH_2=CH_2$(12%)	
			43	$Ph_2PC_2H_4PPh_2$(34%); $CH_2=CH_2$(33%)		

[a] As determined by ^1H n.m.r. spectroscopy. The parentheses contain the estimated percentage product relative to the amount of phosphine present at time 0 (estimated by multiple ^1H n.m.r. integration.) [b] Products which may be produced in the reaction, but not positively identified. [c] Produced by photolysis of Ph_2MeP (see reaction 3), independently from other processes. [d] Extended irradiation after addition of sufficient thiol to react completely with the $Ph_2P(S)CH_2PPh_2$ produced in the reaction. [e] The diphosphine had reacted completely within this time period.

TABLE 2

N.m.r. characteristics

Compound	N.m.r. characteristics[a]	Literature Values (solvent)[b]
Ph_2MePS	CH_3, 1.77(d); $^2J_{PH}$ 13.2 Hz	
Ph_2MeP	CH_3, 1.37(d); $^2J_{PH}$ 3.9 Hz	
$PhMe_2PO$	CH_3, 1.15(d); $^2J_{PH}$ 12.8 Hz	
$Ph_2(PhCH_2)PS$	CH_2, 3.52(d); $^2J_{PH}$ 13.6 Hz	CH_2 3.59(d); $^2J_{PH}$ 13.0 Hz ($CDCl_3$)[c]
$Ph_2P(S)CH_2P(S)Ph_2$	CH_2, 3.85(t); $^2J_{PH}$ 13.6 Hz	
$Ph_2P(S)CH_2PPh_2$	CH_2, 3.25(d/d); $^2J_{P(III)H}$ 0.8 Hz, $^2J_{P(V)H}$ 12.4 Hz	
$Ph_2PCH_2PPh_2$	CH_2, 2.80(t); $^2J_{PH}$ 1.9 Hz	
$Ph_2(MeS)PS$	CH_3, 2.00(d); $^2J_{PH}$ 14.6 Hz	CH_3, 2.21(d); $^2J_{PH}$ 14.7-15.7 Hz ($CDCl_3$)[d]
$Ph_2(MeSCH_2)PS$	CH_2, 3.10(d); $^2J_{PH}$ 7.4 Hz CH_3, ?	CH_2, 3.39(d); $^2J_{PH}$ 8 Hz CH_3, 2.05(s) ($CDCl_3$)[e]
$Ph_2P(S)C_2H_4P(S)Ph_2$	CH_2, 3.00(d); $^2J_{PH}$ 2.0 Hz	
$Ph_2P(S)C_2H_4PPh_2$	CH_2, 2.57(d); $^2J_{PH}$ 3.0 Hz[f]	
$Ph_2PC_2H_4PPh_2$	CH_2, 2.20(t); $^2J_{PH}$ 4.2 Hz	
$PhCH_3$	CH_3, 2.12(s)	
$(PhCH_2)_2$	CH_2, 2.75(s)	

contd/.

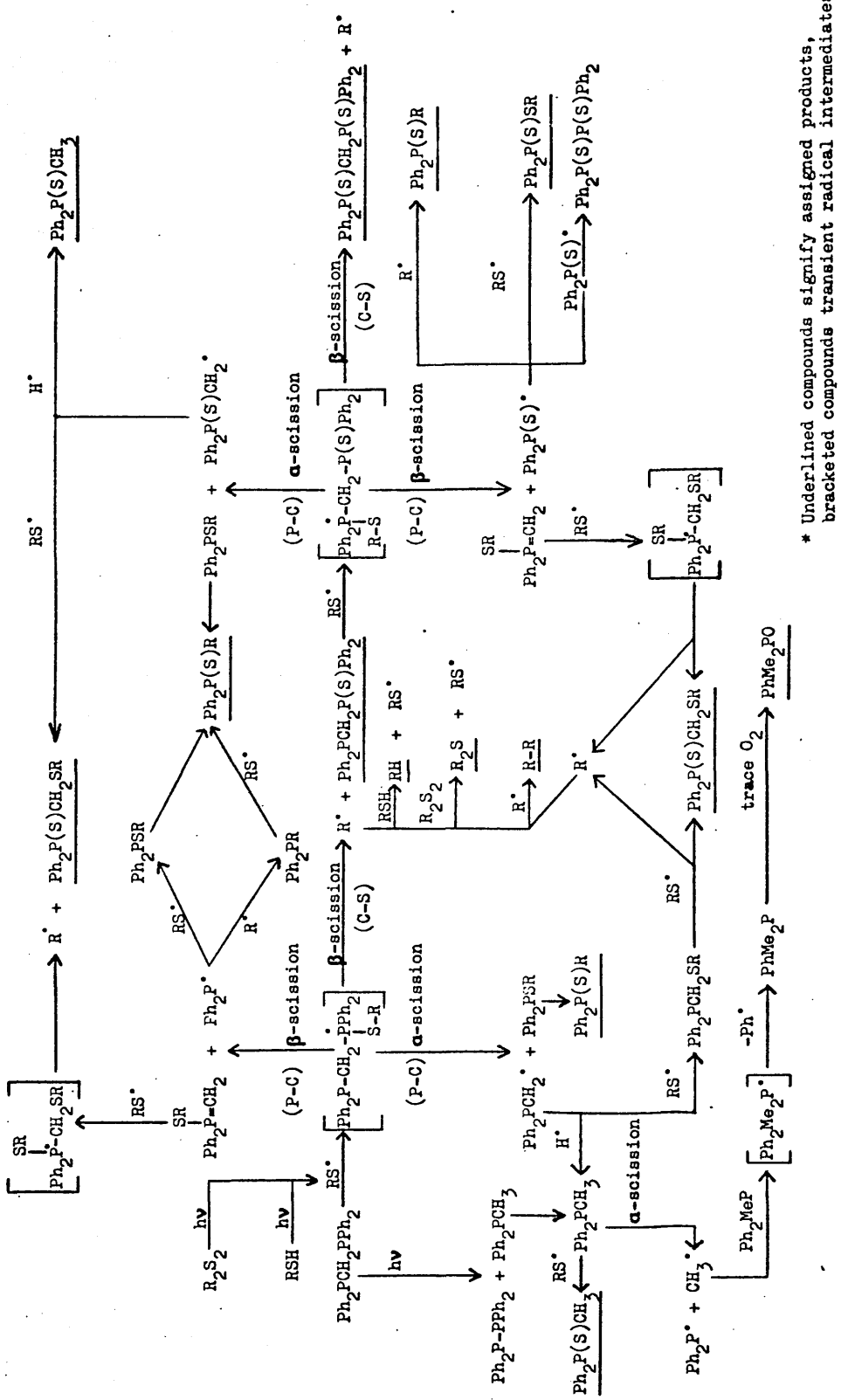
TABLE 2 (Contd.)

Compound	N.m.r. characteristics[a]	Literature Values (solvent)[b]
Me_2S_2	CH_3, 1.97(s)	
Me_2S	CH_3, 1.73(s)	
$CH_2=CH_2$	CH_2, 5.25(s)	
$(PhCH_2)_2S_2$	CH_2, 3.37(s)	
$(PhCH_2)_2S$	CH_2, 3.25(s)	CH_2, 3.42(s) (CCl_4)[g]

[a] In C_6D_6. Proton chemical shifts (δ/p.p.m.) relative to internal $SiMe_4$. (s)=singlet, (d)=doublet, (t)=triplet, and (d/d)=doublet of doublets. [b] Proton chemical shifts (δ/p.p.m.), relative to internal $SiMe_4$, listed only for those compounds which could not be identified by comparison with an authentic sample.

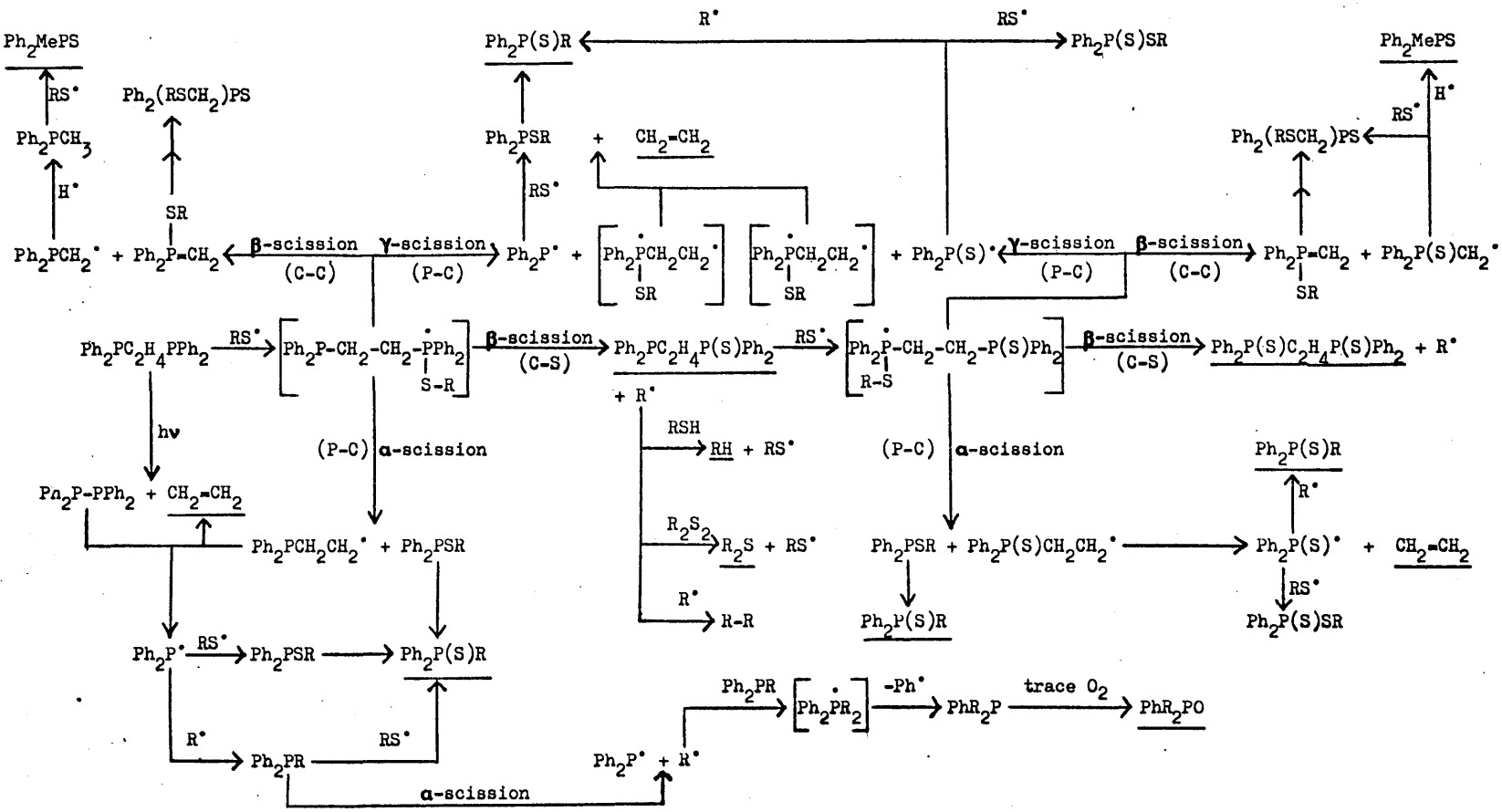
[c] A.W. Verstuyft, D.A. Redfield, L.W. Cary, and J.H. Nelson, Inorg. Chem., 1977, 16, 2776. [d] G. Mavel, R. Mankowski-Favelier, and T.N. Tanh, J. Chim. Phys., 1967, 64, 1692. [e] D.J. Peterson, J. Org. Chem., 1967, 32, 1717. [f] Appeared in most cases as a fairly broad, poorly-resolved doublet. [g] M.G. Voronkov, A.N. Pereferkovich, and V.A. Pestunovich, J. Struct. Chem., 1968, 9, 545.

Scheme 3. Possible Routes to Products in the Photolysis of $Ph_2PCH_2R^1$ (R^1=H,PPh_2,P(S)Ph_2) with RSH or R_2S_2*



* Underlined compounds signify assigned products, bracketed compounds transient radical intermediates

Scheme 4. Possible Routes to Products in the Photolysis of $Ph_2PC_2H_4PPh_2$ with RSH or R_2S_2*



* Underlined compounds signify assigned products, bracketed compounds transient radical intermediates.

formation of 74% Ph_2MePS may not then indicate that β-scission is the more favourable process in this reaction, although, from a consideration of the relative strengths of the P-C and C-S bonds involved, and taking into consideration the energy obtained from P=S bond formation, rupture of the C-S bond (β-scission) would be predicted to occur preferentially.

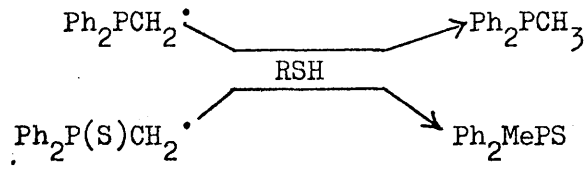
The tentative assignment of the doublet centred at δ1.15(J=12.8 Hz) to $PhMe_2PO$ (Table 2) which appears in reactions 1,4, and 12 was confirmed by the observation of the same doublet when the phosphine, Ph_2MeP, was photolysed alone (Table 1; reaction 3). Traces of $PhMe_2P$ were also detected in this reaction, indicating perhaps that α-scission of Ph_2MeP has produced the relatively stable $Ph_2P^{\bullet}$ radical (which may dimerise to give Ph_2PPPh_2) and the $Me^{\bullet}$ radical. The latter radical may then attack another molecule of Ph_2MeP to produce the phosphoranyl radical $Ph_2Me_2P^{\bullet}$ which can decompose to $PhMe_2P$ by the elimination of a $Ph^{\bullet}$ radical. Kaufman and Griffin[37] isolated small amounts of Ph_2PH and biphenyl when a benzene solution of triphenylphosphine was photolysed in the absence of oxygen. They also stated that the photochemical decomposition of Ph_2PCH_2Ph (to give $Ph_2P^{\bullet} + PhCH_2^{\bullet}$) was faster than that of Ph_3P (to give $Ph_2P^{\bullet} + Ph^{\bullet}$),[38] and therefore we would expect the elimination of a methyl radical from Ph_2MeP to proceed at an intermediate rate.

The autoxidation of tertiary phosphines by molecular oxygen is known to be catalysed by u.v. light,[39] and therefore $PhMe_2P$ must be particularly susceptible to oxidation by small amounts of oxygen present in the reaction medium so that no $PhMe_2P$ is detectable at any time during reactions 1,4 and 12 and only traces are observed when Ph_2MeP is photolysed alone (reaction 3).

The photochemical decomposition of Ph_2MeP to $PhMe_2PO$ only occurs to a small extent in those reactions in which the decomposition of the phosphoranyl radical, R^1_3PSR, is slow (R^1_3=Ph_2Me; R=Me). No such decomposition is observed when R=$PhCH_2$, and therefore it is clear that the photochemical decomposition of Ph_2MeP will have very little effect on the overall reaction between tertiary phosphines and thiols or disulphides.

Reaction 2 indicates that for R=$PhCH_2$, **β**-scission occurs approximately nine times more readily than **α**-scission.

Extended irradiation of $Ph_2PCH_2PPh_2$ with Me_2S_2 (reaction 4) results in the formation of Ph_2MePS to a very large extent. After photolysis for 4 h, however, it is clear that both **α**- and **β**-scission are taking place, the former producing Ph_2PCH_3 and Ph_2PSMe, which both eventually lead to the formation of Ph_2MePS (see scheme 3), the latter producing $Ph_2P(S)CH_2PPh_2$ which is subject to further reaction with Me_2S_2 leading to the formation of more Ph_2MePS (as reaction 8 indicates). Interestingly, no $Ph_2P(S)CH_2P(S)Ph_2$ was detected in this reaction. This diphosphine was also subject to substantial **α**-scission with benzyl thiol (reaction 5) resulting once again in the formation of Ph_2MePS as a major product after 66 h irradiation. It should be noted, however, that after 12 h irradiation there was twice as much $Ph_2P(S)CH_2PPh_2$ formed as Ph_2MePS, the former producing only 18% $Ph_2P(S)CH_2P(S)PPh_2$ on extended irradiation. The hydrogen transfer ability of the thiol may favour the **α**-scission process, since the $Ph_2PCH_2^{\bullet}$ and $Ph_2P(S)CH_2^{\bullet}$ radicals may conveniently receive a hydrogen atom from the thiol (equation 39).



(39)

Thus, when $Ph_2PCH_2PPh_2$ is photolysed along with $(PhCH_2)_2S_2$ (reaction 6), the major product is $Ph_2P(S)CH_2P(S)Ph_2$ (54%) and only 20% Ph_2MePS is produced, there being no readily available hydrogen atoms in the reaction mixture.

Reaction 8 also indicates the relative importance of (P-C) **α**- and **β**-scission when (C-S) **β**-scission is slow, by the observation of signals attributable to $Ph_2(MeS)PS$ and $Ph_2(MeSCH_2)PS$ (see scheme 3).

Reactions 9 and 10 confirm, however, that for $R=PhCH_2$ the preferred decomposition mode for $Ph_2P(S)CH_2\dot{P}(SR)Ph_2$ is **β**-scission resulting in the formation of $Ph_2P(S)CH_2P(S)Ph_2$ (almost quantitatively in reaction 10).

Reactions 12 and 13, involving the photochemical reaction of $Ph_2P-C_2H_4-PPh_2$ with Me_2S_2 or $(PhCH_2)_2S_2$, give contrasting results in that in reaction 12 the diphosphine has reacted completely within 3 h producing Ph_2MePS, Ph_2MeP and $Ph_2P(S)C_2H_4P(S)Ph_2$ as the major products whereas in reaction 13 there still remains 64% unreacted diphosphine after irradiation for 6 h. After extended irradiation (43 h), 16% diphosphine still remained and no Ph_2MePS or $Ph_2P(S)CH_2Ph$ had been produced. Apparently no **α**-scission has occurred at all in reaction 13 and the **β**-scission reaction is unusually slow. In reaction 12, the amount of ethylene produced in the first 3 h of photolysis is at least twice as much as is produced in both reactions 13 and 14 after 6 h irradiation. This might imply that the **α**- and **γ**-scission processes for the decomposition of the intermediate phosphoranyl radical (see scheme 4) may be favoured over **β**-scission since both produce the

relatively stable $Ph_2P^{\bullet}$ radicals which can react with $MeS^{\bullet}$ and $Me^{\bullet}$ to produce Ph_2MePS (after isomerisation) and Ph_2MeP, respectively. It is not clear, however, why no **α**- or **γ**-scission occurs in reaction 13, since the **β**-scission is certainly not a fast reaction.

In conclusion, then, it would appear that **β**-scission is the most important decomposition route for the phosphoranyl radical intermediate $Ph_2\dot{P}(SR)R^1$, when $R^{\bullet}$ is an easily formed radical. When, however, $R^{\bullet}$ is less readily formed, and $R^1=(CH_2)_nP(X)Ph_2$ (n=1,2; X=: or S), C-P scission (which could be **α**, **β** or **γ** depending on n) begins to predominate, although (C-S) **β**-scission still occurs to an appreciable extent in each case.

When all four decomposition modes occurred together, the problem of identifying all the products became acute and it was not always possible to determine with complete confidence the separate products arising from the different reaction pathways. Proton n.m.r. spectroscopy, although a convenient and powerful reaction monitor, might not always be the best means for product identification, and other techniques might be better applied to elucidate the more complex reactions described above.

(c) Photochemical Reactions between Tertiary Phosphines and Organic Diselenides.

As mentioned earlier, Chu and co-workers[25] recently reported a quantitative study on the photolysis of dibenzyl diselenide in acetonitrile or benzene (equation 40 ; R=CH_2Ph).

$$R_2Se_2 \xrightarrow{h\nu} R_2Se + Se \qquad (40)$$

They proposed equations (29), (32), and (41)-(44) (R=CH_2Ph) to account for their observations.

$$R_2Se_2 \xrightarrow{h\nu} R^\bullet + RSe_2^\bullet \qquad (41)$$

$$RSe_2^\bullet \longrightarrow RSe^\bullet + Se \qquad (42)$$

$$R^\bullet + RSe^\bullet \longrightarrow R_2Se \qquad (43)$$

$$2RSe^\bullet \longrightarrow R_2Se_2 \qquad (44)$$

An e.s.r. study on u.v.-irradiated diphenyl diselenide (in the gas phase) has also been reported by Schmidt and co-workers[19] and indicates the formation of $PhSe^\bullet$ and $PhSe_2^\bullet$ radicals. In contrast, the photochemical cleavage of sulphur-carbon bonds in organic disulphides is well known, although it tends to be important only if the carbon radicals produced are stabilised (e.g. R=CH_2Ph, ^tBu)[40]. Also it should be noted that the photochemistry of dibenzyl disulphide is well documented, and does not lead to deposition of sulphur[40].

According to Chu et al., in the photolysis of R_2Se_2, initially formed $RSe^\bullet$ radicals (equation 29) may recombine (equation 44) or attack the weak Se-Se linkage leading to radical displacement and reformation of R_2Se_2. Neither of these reactions would produce the observed products. Therefore equation (41) is the most probable step leading to the formation of the observed photolysis products.

They confirmed the presence of benzyl radicals in the photolysis

of $(PhCH_2)_2Se_2$ by the formation of benzyl chloride upon irradiation of the diselenide in carbon tetrachloride. The generation of benzyl radicals also indicated the concomitant formation of the $PhCH_2Se_2^{\bullet}$ radical as an essential step leading to the deposition of elemental selenium.

This study by Chu and co-workers poses the question whether the phosphine selenide produced from Et_2Se_2 and Ph_2MeP[27] was formed by the cyclic chain mechanism (equations 29-32) (p.14), or by the operation of reaction (40) followed by reaction (45) of the phosphine with elemental selenium.

$$Ph_2MeP + Se \longrightarrow Ph_2MePSe \qquad (45)$$

This latter step is well documented[41].

We have examined the reactions of several diselenides, R_2Se_2 ($R=PhCH_2$,Et,Me,Ph), and tertiary phosphines, R^1_3P($R^1_3=Me_2Ph,MePh_2,Ph_3$), using ^1H n.m.r. spectroscopy to monitor their progress.

Little is known about the photochemistry of selenium compounds. We have recorded the u.v. spectra of some diselenides and find that the lowest-energy absorption of each of these diselenides is in the range 300-335 nm (Table 3).

TABLE 3

Lowest-energy u.v. absorption of the diselenides in cyclohexane

Compound	λmax./nm	$10^{-3}\varepsilon$/l mol^{-1} cm^{-1}
$Se_2(CH_2Ph)_2$	304	0.75
Se_2Et_2	310	1.12
Se_2Me_2	317	0.47
Se_2Ph_2	332	1.03

This band is analogous to the bond-rupturing $n \longrightarrow \sigma^*$ (or $\pi^* \longrightarrow \sigma^*$, depending on the dihedral angle) transition of organic disulphides.[42]

Both pyrex and deuteriobenzene are transparent in this region.

The reaction between Ph_2MeP and dibenzyl diselenide produced Ph_2MePSe (100), $Se(CH_2Ph)_2$ (53), and bibenzyl (16%), with some unchanged $Se_2(CH_2Ph)_2$ (10%), and was essentially complete after irradiation for 30 min. Under identical conditions, a slower reaction of $Se_2(CH_2Ph)_2$ alone proceeded to only 5% completion. The slower reaction could not be accounted for by scattering of light by the selenium produced, as experiments in u.v. cells showed that there was not a significant decrease in transmittance at 304 nm in the reaction periods employed between monitoring the reaction (5 min). Furthermore, careful removal of the selenium from the n.m.r. tube produced no measurable increase in reaction rate. Thus in the reaction time available no more than about 5% of the Ph_2MePSe produced would have been formed from a reaction of Ph_2MeP and elemental selenium.

The observation of bibenzyl among the reaction products of Ph_2MeP and $(PhCH_2)_2Se_2$ is significant. None was found by us, nor reported by Chu and co-workers[25], in the photolysis of $(PhCH_2)_2Se_2$ alone. The bibenzyl is presumably formed by the coupling of benzyl radicals (equation 46; R=CH_2Ph).

$$2R^{\bullet} \longrightarrow R_2 \qquad (46)$$

Benzyl radicals will be involved in the chain-propagation cycle (equations 30-32; R=CH_2Ph) for the formation of Ph_2MePSe, whereas their role in the photolysis of $(PhCH_2)_2Se_2$ alone is less important (this is not a chain reaction). The low reactivity of benzyl radicals probably favours reaction (46) at the expense of (32). Similar observations have been reported for the reaction between $S_2(CH_2Ph)_2$ and $(EtO)_3P$[4].

We therefore conclude that the bulk of the phosphine selenide at least is produced <u>via</u> reactions (30)-(32), involving the phosphoranyl

radical intermediate ($Ph_2MePSeCH_2Ph$), and reactions (43),(44), and (46) act as chain terminators. The benzylselenyl radicals, $PhCH_2Se$, responsible for the chain process can be formed directly by Se-Se cleavage (equation 29; R=$PhCH_2$) or indirectly by C-Se cleavage (equation 41 followed by 32 and 42). The production of 16% of bibenzyl means that chain-termination steps account for at least 16% of the benzyl-containing products (steps 43 and 44 cannot be independently monitored). This requires that the photo-chemical initiation steps must act on at least 16% of $Se_2(CH_2Ph)_2$. Carbon-selenium cleavage, leading to $Se(CH_2Ph)_2$ and Se, proceeds only 5% in 30 min, however, so the more important initiation step must be selenium-selenium cleavage.

Subsequent to our work, Chu and Marsh[43] confirmed our results in a short communication where they stated that direct photolysis of $Se_2(CH_2Ph)_2$ in the presence of Ph_3P at 313 and 366 nm in acetonitrile or benzene resulted in the production of $(PhCH_2)_2Se$, bibenzyl, and Ph_3PSe. The quantum yields for the disappearance of the diselenide were found to increase with increasing concentration of Ph_3P from $\Phi = 0.16$ with no Ph_3P present to $\Phi = 6.80$ with a twofold excess of the phosphine. The large quantum yields were thought to provide strong evidence for a free-radical chain reaction. They also found that irradiation of the diselenide in the absence of Ph_3P resulted in less than 7% decomposition of $Se_2(CH_2Ph)_2$ after 3 h exposure, whereas in the presence of Ph_3P, under identical conditions, the diselenide reacted completely within 1 h. They, therefore, revised their earlier assertions and stated that the major primary photoprocess must be facile Se-Se cleavage, in keeping with our results.

Before discussing the reactions of other diselenides, three other radical processes, (47-49), might be considered.

$$RSe^{\bullet} + R_2Se_2 \longrightarrow SeR_2 + RSe_2^{\bullet} \qquad (47)$$

$$RSe_2^{\bullet} + Ph_2MeP \longrightarrow Ph_2\overset{\bullet}{M}eP(Se_2R) \qquad (48)$$

$$Ph_2\overset{\bullet}{M}eP(Se_2R) \longrightarrow Ph_2MePSe + RSe^{\bullet} \qquad (49)$$

Any participation of (47) must be limited, since it would convert the photochemical decomposition of $Se_2(CH_2Ph)_2$ into a chain reaction. The quantum yield for this process (0.16)[25] suggests that this is not so. This in turn means that steps (48) and (49) can only contribute 5% or less (the maximum contribution of step 41) to the reaction between $Se_2(CH_2Ph)_2$ and Ph_2MeP. Radical-termination steps forming $RSe_nR(n > 2)$ can also be envisaged, (Lardon[26] detected dibenzyl polyselenides in a ^1H n.m.r. investigation of the thermal decomposition of $Se_2(CH_2Ph)_2$) but no such polyselenides were detected in any of our experiments.

The reactions of several other diselenides and tertiary phosphines were examined. All proceeded smoothly under u.v. irradiation to give phosphorus (V) selenides and organic monoselenides, SeR_2, although requiring a longer reaction time than $Se_2(CH_2Ph)_2$ and Ph_2MeP (see Table 4).

TABLE 4

Relative times of irradiation producing 50% reaction between tertiary phosphines and diselenides

Phosphine	Diselenide	t/h
$PMePh_2$	$Se_2(CH_2Ph)_2$	0.25
$PMePh_2$	Se_2Et_2	1.5
$PMePh_2$	Se_2Me_2	6.0
$PMePh_2$	Se_2Ph_2	60
PMe_2Ph	Se_2Me_2	2.5
PMe_2Ph	Se_2Ph_2	40
PPh_3	Se_2Me_2	13

Under identical conditions, none of the other diselenides alone produced measurable amounts of selenium and SeR_2. This would be expected, since C-Se cleavage would be less facile for these organic radicals[40]. Thus the operation of the radical chain route involving the phosphoranyl intermediates $R^1_3P^{\bullet}(SeR)$ appears to apply generally to all the reactions of tertiary phosphines and diselenides studied.

There are at least two explanations for the variations in reaction times (Table 4). First, the rate of Se-Se cleavage to generate $RSe^{\bullet}$ may vary. This will require the slower-reacting diselenides to have available more efficient non-dissociative pathways to reattain their ground states after absorbing u.v. radiation. Secondly, the rate-determining step may be the elimination of a carbon radical from the phosphoranyl intermediates (reaction 31). If this is slow, α-scission of P-Se (the reverse of 30) will compete more favourably and lead <u>via</u> (44) to the reformation of the starting compounds. We earlier showed that carbon-radical elimination is critical in the reaction of thiyl radicals with tertiary phosphines[30].

We marginally favour the second interpretation. The different reaction rates observed for different phosphines (PMe_2Ph › $PMePh_2$ › PPh_3) are difficult to rationalise in terms of control by step (29). Also, the effect of organic groups (CH_2Ph › Et › Me › Ph) is consistent with increasing energy of radical formation[30]. Attempts to confirm this by examining other photochemical reactions of diselenides failed, however. No reaction was observed between Se_2Ph_2 and either $PhMeC{=}CH_2$ or $PhC{\equiv}CH$ after irradiation for 40 h , and ^1H n.m.r. spectroscopy failed to detect any mixed diselenides after irradiation of Se_2Me_2 + Se_2Ph_2 or Se_2Me_2 + Se_2Et_2 for 20 h. A reaction, however, did occur between Se_2Et_2 and Ph_2Se_2, (equation 50; R=Et,R^1=Ph), but it also proceeded (rather more slowly) in the absence of u.v. irradiation.

$$R_2Se_2 + R^1_2Se_2 \rightleftharpoons 2\ RSeSeR^1 \qquad (50)$$

The former failure is understandable in view of the likely reversible nature of the reaction and the difficulties encountered in analogous reactions of disulphides[20b]. In fact, in a very recent paper, Scaiano and Ingold[44] reported that they were unable to detect any selenoalkyl radicals using e.s.r. spectroscopy in the attempted photochemical reaction between dimethyl diselenide and terminal olefins (equation 51; R=H, ^tBu).

$$Me_2Se_2 \xrightarrow{h\nu} MeSe^\bullet \xrightarrow{CH_2=CR_2} CH_3SeCH_2CR_2^\bullet \qquad (51)$$

They attributed their failure to detect such radicals to a facile, and probably exothermic, β-scission reaction (equation 52; R=H, ^tBu), resulting in the regeneration of the reactants.

$$MeSeCH_2CR_2^\bullet \longrightarrow MeSe^\bullet + CH_2=CR_2 \qquad (52)$$

They were also unable to detect the methylselenyl radical, $MeSe^\bullet$, itself when Me_2Se_2 was photolysed in hydrocarbon solvents nor when mixtures of methyl selenol and di-tert.-butyl peroxide were photolysed. When the diselenide, however, was photolysed in the presence of a radical trap, tert.-butyl phenyl nitrone, $PhCH=N(O)^tBu$, they experienced no trouble in trapping a radical that appeared to be $MeSe^\bullet$. They attributed their failure to detect the methylselenyl radical directly by e.s.r. spectroscopy to the fact that such radicals probably have very short relaxation times and hence extremely broad lines. (Similar difficulties have been experienced in attempts to detect alkyl-thiyl radicals in solution using e.s.r. spectroscopy[45].)

The failure to detect any mixed diselenides is difficult to interpret, although variable results have been reported for irradiation experiments on mixtures of disulphides[46]. Irradiation of an equimolar mixture of Me_2S_2 and Et_2S_2, for example, gave ethyl methyl disulphide as the sole detectable product. On irradiating mixtures of Me_2S_2 and

$^{n}Pr_2S_2$ or Et_2S_2 and $^{n}Pr_2S_2$, however, a dramatic decrease in the efficiency of the disulphide exchange reaction was observed, which seemed to indicate a reduced susceptibility of $^{n}Pr_2S_2$ itself to the exchange[46]. Also, attempts to prepare methyl-t-butyl and ethyl-t-butyl disulphides by irradiation of mixtures of the corresponding symmetrical disulphides have been completely unsuccessful[47].

McFarlane[48] prepared methyl phenyl diselenide, PhSeSeMe, by mixing equimolar proportions of PhSeH and Me_2Se_2 at room temperature and confirmed that an equilibrium had been established (equation 53), by pumping off the volatile methyl selenol, which was identified by its ^{1}H n.m.r. spectrum.

$$PhSeH + Me_2Se_2 \rightleftharpoons PhSeSeMe + MeSeH \qquad (53)$$

An essentially pure sample of PhSeSeMe was obtained by this means, but attempts to distil it gave only Me_2Se_2 and Ph_2Se_2 (54).

$$2\ PhSeSeMe \xrightarrow{\Delta} PhSeSePh + MeSeSeMe \qquad (54)$$

This result might explain our failure to observe any PhSeSeMe when we irradiated a mixture of Me_2Se_2 and Ph_2Se_2, since it would appear that the equilibrium, (equation 50; R=Me,R^1=Ph,Et), may lie completely over on the side of the symmetrical diselenides.

It should be noted, however, that McFarlane ascribed a singlet only 0.03p.p.m. downfield of the Me_2Se_2 singlet to the methyl protons of PhSeSeMe, and, therefore, it is possible that the mixed diselenides, PhSeSeMe and EtSeSeMe, were indeed produced by us to some extent, but were not detected by a chance coincidence of the chemical shifts of symmetric and asymmetric diselenides in deuteriobenzene solution. In the one system which did exchange (Ph_2Se_2/Et_2Se_2), only the triplet appearing approximately 0.07p.p.m. upfield from the methyl protons of Et_2Se_2 indi-

cated any exchange taking place; the methylene proton signals remained unchanged. (The equilibrium was reached after about 30 min irradiation or after standing for 4 h and it did not go to completion but stopped when an approximately 60:40 mixture of unsymmetrical to symmetrical diselenide was reached.)

A ^{1}H n.m.r. investigation of the photochemically-initiated reaction between $Ph_2PCH_2PPh_2$ and Me_2Se_2 was also carried out and the major products were obviously those arising from **a**-scission of the intermediate phosphoranyl radical; it was not possible, however, to confirm the exact nature of the products, but it appeared that very little Ph_2MePSe had been produced (Ph_2MePS was the major product in the equivalent reaction with Me_2S_2). This result can be explained by the known reluctance of Ph_2PSeMe (produced by **a**-scission of $Ph_2\dot{P}(SeMe)CH_2PPh_2$) to undergo rearrangement to Ph_2MePSe[49]. Further reaction of Ph_2PSeMe with Me_2Se_2 should yield $Ph_2P(Se)SeMe$ as a major product. A doublet centred at **δ** 2.7 ($^3J_{PH}$= 14.3Hz) might be assigned to $Ph_2P(Se)SeMe$ (although $Ph_2P(S)SMe$ in C_6D_6 was thought to be at **δ** 2.0).

The observation of products attributable to **a**-scission of the phosphoranyl radical in the $Ph_2PCH_2PPh_2/Me_2Se_2$ system, prompted us to have a closer look at the minor products in the reactions between the various diselenides and tertiary phosphines described earlier. Signals, previously thought to be insignificant, spurious resonances in the ^{1}H n.m.r. spectra of the products of these reactions, could be assigned in the light of the above observation, to products arising from the **a**-scission of the intermediate phosphoranyl radical, $R^1_3\dot{P}(SeR)$ (equation 55; R^1_3=Ph_3,Ph_2Me,$PhMe_2$ and R=Ph,Me,Et,$PhCH_2$).

$$R^1_3\dot{P}(SeR) \xrightarrow{\textbf{a}\text{-scission}} R^1_2PSeR + R^{1\cdot} \qquad (55)$$

These signals, however, accounted for less than 10% of the total reaction products, and appeared mostly in those reactions where β-scission was relatively slow (Table 4; t ≫ 6 h). The α-scission of the selenophosphoranyl radical intermediate, $R^1_3\dot{P}SeR$, thus, does not interfere significantly with the major decomposition pathway, β-scission. Therefore our earlier conclusions on the photochemical reactions between tertiary phosphines and organic diselenides are still valid.

Once again, it would appear that the relative importance of α- or β-scission is dependent upon the strengths of the C-P and, in this case, C-Se bonds undergoing scission. When R^1=Ph or Me, very little α-scission occurred because of the strength of the P-C bonds in these phosphines, whereas when R^1=CH_2PPh_2, α-scission became more important, indicating perhaps the reduced P-C bond strength in methylene-bridged diphosphines and the increased stability of the radical, $Ph_2PCH_2^{\bullet}$ (which may be resonance-stabilised by delocalisation of the unpaired electron into the vacant d-orbitals on phosphorus) so produced.

(d) Photochemical Reactions between Tertiary Phosphines and Organic Ditellurides.

Solutions of both dibenzyl ditelluride or diethyl ditelluride reacted quantitatively under u.v. irradiation to produce tellurium and the monotelluride (equation 56; R=$PhCH_2$,Et).

$$R_2Te_2 \xrightarrow{h\nu} R_2Te + Te \qquad (56)$$

Presumably steps analogous to those reported by Chu[25] for the photodecomposition of dibenzyl diselenide (equations 41-43, and 32) operate, initiated by cleavage of tellurium-carbon bonds. The benzyl derivative photolysed more rapidly than the ethyl compound (times to 50% reaction are given in Table 5), and both reacted more rapidly than their selenium analogues. These relative rates would be expected from the ease of

cleavage of the element-carbon bonds.

When the ditellurides were photolysed in the presence of diphenylmethylphosphine, the monotelluride and tellurium metal were again produced, but at a slightly faster rate (Table 5).

TABLE 5

Relative Reaction Times

Reactants	Time to 50% reaction[a] (min)
$(PhCH_2)_2Te_2$	13.5
$(PhCH_2)_2Te_2$ + Ph_2MeP	9
$(PhCH_2)_2Te_2$ + $Ph_2PCH_2PPh_2$	12
Et_2Te_2	150
Et_2Te_2 + Ph_2MeP	105

([a] Values quoted are the mean of two closely comparable reactions. Errors are estimated at ± 0.5 min for the $(PhCH_2)_2Te_2$ reactions, but ± 30 min for the Et_2Te_2 reactions owing to the difficulty of accurately integrating partly overlapping signals in the ^1H n.m.r. spectra.)

Tellurium deposition on the walls of the reaction tubes continued for some time after irradiation was interrupted. These differences can be accounted for by the formation of some diphenylmethylphosphine telluride. Phosphine tellurides are known to be unstable when aryl groups are attached to phosphorus, and their decomposition to phosphine and tellurium is accelerated by glass surfaces (equation 57)[50,51].

$$Ph_2MePTe \longrightarrow Ph_2MeP + Te \qquad (57)$$

No separate ^1H n.m.r. signals for Ph_2MePTe were observed, but the methyl doublet of Ph_2MeP was found to shift downfield with reduced coupling constant (sometimes to zero) during and after irradiation of the R_2Te_2/Ph_2MeP mixtures, indicating the establishment of a rapid equilibrium between Ph_2MeP and Ph_2MePTe (equations 58 and/or 59).

$$Ph_2MePTe + Ph_2MeP \rightleftharpoons Ph_2MeP + Ph_2MePTe \quad (58)$$

$$Ph_2MePTe \rightleftharpoons Ph_2MeP + Te \quad (59)$$

Variable temperature n.m.r. measurements on these reaction products and on mixtures of Ph_2MeP and powdered tellurium showed that the phenomenon was temperature dependent (see Chapter 3, p. 95f), but failed to give reproducible results, probably due to the heterogeneous nature of the system.

Mixtures of $(PhCH_2)_2Te_2$ and Ph_2MeP deposited tellurium even after very short irradiation periods, but no free tellurium was apparent after irradiating Et_2Te_2 and Ph_2MeP for up to 120 minutes, although the methyl doublet of the phosphine was again narrowed and shifted downfield. This suggested that either the tellurium depicted in equilibrium (59) remained in solution, or that it could be transferred from phosphorus to phosphorus by a bimolecular route and was never completely released (equation 58). (Linear intermediates of the type $R_3P\text{-}Te\text{-}PR_3$ ($R={}^tBu, Me_2N$) were recently proposed to account for the rapid transfer of tellurium in the system R_3PTe/PR_3 [52].) To test the latter possibility, mixtures of $Ph_2PCH_2PPh_2$ and Et_2Te_2 were irradiated briefly and examined, in the hopes of finding intramolecular transfer. The deuteriobenzene solutions remained clear, but the entire methylene triplet of the diphosphine was partially collapsed and moved downfield. Thus the tellurium transfer involves intermolecular migration in this case also and we are unable to distinguish which mechanism operates. Longer irradiation of either Ph_2MeP/Et_2Te_2 or $Ph_2PCH_2PPh_2/Et_2Te_2$ leads to the deposition of tellurium, as does even brief irradiation of mixtures of $Ph_2PCH_2PPh_2$ and $(PhCH_2)_2Te_2$. Also, the clear solutions resulting from short irradiations deposit tellurium on standing.

The phosphine tellurides may be produced by the operation of steps analogous to reactions (30) and (31) involving $RTe^{\bullet}$ radicals, or by dir-

-ect reaction of the phosphine and elemental tellurium[51], (if the latter, the faster reaction rates observed for the decomposition of R_2Te_2 in the presence of R^1_3P would be caused by less light-scattering by deposited tellurium). The reaction between tertiary phosphines and diorganodiselenides proceeds via steps (30) and (31) after the photochemical cleavage of selenium-selenium bonds (see earlier discussion). Even if the phosphine tellurides in this work are formed by the attack of RTe$^\bullet$ on R^1_3P, it seems more likely that the initiation step will be the photochemical cleavage of Te-C (which can lead to RTe$^\bullet$ by steps analogous to 42 and 32) rather than of Te-Te, since, unlike the selenium case, the increase in reaction rate in the presence of tertiary phosphine is not spectacular (Table 5).

It therefore appears that the ease of cleavage of element-carbon bonds by u.v. irradiation increases in the series R_2S_2 < R_2Se_2 < R_2Te_2, whereas the ease of cleavage of element-element bonds is the reverse (although in the case of the disulphides, light of wavelength down to about 250 nm may be needed to excite the bond-rupturing $n\rightarrow\sigma^*$ absorption[42]). Photochemical cleavage of Te-C bonds has been observed in tellurophenes[53]. Interestingly, the monotellurides Et_2Te and $(PhCH_2)_2Te$ also decomposed on prolonged irradiation. In an attempt to isolate and characterise $(PhCH_2)_2Te$ by irradiating solutions of the ditelluride alone it was discovered that although $(PhCH_2)_2Te$ was produced in the early stages of photolysis, at no time was it possible to obtain complete reaction of the ditelluride without producing substantial amounts of bibenzyl. Similarly, ethylene was identified (by comparison of n.m.r. signals with those of an authentic sample) as a by-product from the prolonged photolysis of Et_2Te_2, with or without added phosphine.

Subsequently, Spencer and Cava[54] reported in a note some chemical reactions of dibenzyl ditelluride involving extrusion of tellurium.

They found that u.v. irradiation of the ditelluride in deuteriochloroform under nitrogen resulted in the rapid deposition of tellurium and the formation of dibenzyl monotelluride (equation 60).

$$(PhCH_2)_2Te_2 \xrightarrow{h\nu} (PhCH_2)_2Te + Te \qquad (60)$$

They did not apparently detect any bibenzyl, even when irradiation continued for four hours beyond the complete decomposition of the ditelluride, indicating, in contrast to our results, that the monotelluride was relatively stable under their reaction conditions. They also thermally decomposed $(PhCH_2)_2Te_2$ by heating it without solvent at 120°C for ten minutes under nitrogen. Again, dibenzyl telluride and tellurium were the only products detected. This was found to be in contrast to the attempted thermal decomposition of the analogous diselenide under the same conditions, the diselenide being recovered completely unchanged. Thermal decomposition of dibenzyl diselenide is known to occur at temperatures above 150°C[26].

Experimental

N.m.r. spectra were recorded on Varian T-60, Varian HA-100, or JEOL C-60HL instruments. Proton chemical shifts are relative to internal $SiMe_4$. Phosphorus chemical shifts are relative to external H_3PO_4 (positive shifts are downfield from H_3PO_4). Mass spectra were recorded on an AEI MS12 spectrometer. Ultraviolet-visible spectra were recorded on a Unicam SP 800B spectrophotometer, infrared spectra on Perkin-Elmer 225 and Perkin-Elmer 580 instruments.

The various phosphines used in this work were obtained commercially from Strem Chemicals Inc., Fluorochem Ltd., or the Maybridge Chemical Company. The thiols and disulphides were supplied by Koch-Light Laboratories Ltd., and Me_2Se_2 was obtained commercially from Strem Chemicals Inc. The Aldrich Chemical Co., Ltd. supplied 1,3-propanedithiol, and deuteriobenzene was obtained commercially from CEA-France. The purity of all the commercial products was at least 97% and in most cases $\geq$ 99%. Their purity was further confirmed from their respective n.m.r. spectra. Diethyl diselenide and dibenzyl ditelluride were prepared by standard methods[55]. $Ph_2PCH_2P(S)Ph_2$ was prepared as described in Chapter 3 (p.105). Dibenzyl diselenide, diphenyl diselenide, and diethyl ditelluride were generously donated by Mr. D.R. Wilson and Mr. T.H. Green of this department.

Photolytic reactions were performed under an atmosphere of nitrogen using a Hanovia medium-pressure mercury lamp (PCR 11). The procedure for placing air-sensitive reactants in a n.m.r. tube typically involved the addition of the non-volatile components (either by weight difference for solids or microlitre syringe for high boiling liquids) prior to evacuating the tube on the vacuum line and then letting the system down to dry nitrogen. Deuteriobenzene/T.M.S. (ca. 0.6 ml) was

added against a counter-current of nitrogen, and the n.m.r. tube was then sealed with a tight-fitting red cap around which a protective strip of Parafilm was placed. In the vast majority of cases, no evidence for oxidation of the reactants or products was noted, and only when the particularly air-sensitive dimethylphenylphosphine was used was there any indication of oxygen abstraction producing $PhMe_2PO$.

A ^1H n.m.r. spectrum of the reactants was obtained immediately prior to photolysis and thereafter as often as was felt to be necessary until the reaction was complete. The n.m.r. tube was strapped to the u.v. lamp using elastic bands and when necessary the system was placed in a water bath, the temperature (285 K) of which was maintained by a continuous flow of water through the bath.

When reactions were carried out in the absence of solvent, the reactants were frozen at liquid N_2 temperatures prior to rigorous degassing using two freeze-thaw cycles. The system was then filled with nitrogen and sealed as outlined above.(No degassing of the deuteriobenzene solutions was usually employed due to frequent breakages of the very thin-walled n.m.r. tubes during the thawing stage.)

All the reactants and ultimate products were known compounds, and their identification from n.m.r. spectra was confirmed either by observing complete superimposition of the resonances with those of authentic samples, or in the absence of authentic samples, by comparing literature chemical shift values (and coupling constants where appropriate) with the observed resonances. Tables 2, 6 and 7 list the relevant n.m.r. characteristics of the reactants and products involved in the various photochemical studies undertaken in Chapter 1 of this thesis.

(a) Reaction of 1,3-propanedithiol with diphenylvinylphosphine (dvp).

A mixture of dvp (1 ml, 6.12 mmol) and 1,3-propanedithiol (0.33g, 3.06 mmol) was irradiated with u.v. light for 19 h in a Pyrex vessel. Any volatile materials were removed by pumping, to leave as final product a pale yellow, viscous liquid, the ^{1}H and ^{31}P n.m.r. spectra of which indicated that $Ph_2P(S)C_2H_4S^nPr$ was the major product in a mixture of compounds.

N.m.r. tube reaction.

A mixture (2:1) of dvp (0.46 ml, 2.38 mmol) and 1,3-propanedithiol (0.129g, 1.19 mmol) was irradiated in a n.m.r. tube for 3 h. The ^{31}P n.m.r. showed the presence of unreacted dvp (δ,-11.1 p.p.m.) and an unidentified compound, the chemical shift of which, (δ,-17.5 p.p.m.), was typical of P(III) compounds with the general formula, $Ph_2PC_2H_4SR$.[30] No P(V) compounds were detected at this stage but further irradiation must have led to the formation of $Ph_2P(S)C_2H_4S^nPr$ as described in the above reaction.

(b) The Reaction of Thiols or Disulphides with Phosphines and/or Olefins

(i) RSH + CH_2=CMePh

1:1 Mixtures (ca. 0.1g scale) of RSH (R=Ph,$PhCH_2$) and α-methyl styrene were photolysed in n.m.r. tubes for 5 h. The ^{1}H n.m.r. spectra of the products indicated that both reactions had produced their respective anti-Markownikov addition products, $RSCH_2CHMePh$, although the reaction with R=Ph appeared to be slightly faster since no reactants remained after 5 h, whereas with R=$PhCH_2$ some unreacted starting materials were observed.

(ii) RSH + CH_2=CMePh + Ph_2MeP

Similarly 1:1:1 mixtures (ca. 0.1g of each component) of RSH (R=Ph,$PhCH_2$) with CH_2=CMePh and Ph_2MeP were photolysed in n.m.r. tubes for

18 h. For R=Ph, only $PhSCH_2CHMePh$ was observed to have been produced, the signal due to the methyl protons of Ph_2MeP was unchanged, and no doublet due to Ph_2MePS was detected. For R=$PhCH_2$, however, substantial amounts of Ph_2MePS and toluene were produced, as well as a small amount of $PhCH_2SCH_2CHMePh$ (ca.25% of products). No products compatible with $PhCH_2^{\bullet}$ radical addition to CH_2=CMePh were detected.

(iii) RSH + CH_2=CMePh + Ph_2MeP in solution

Equivalent concentrations (ca. 0.27 mol l^{-1}) of the tertiary phosphine, Ph_2MeP, the olefin, CH_2=CMePh, and the respective thiols, RSH (R=Ph, ^tBu, $PhCH_2$), in deuteriobenzene were irradiated in Pyrex n.m.r. tubes in a rigorous nitrogen atmosphere. Control experiments on solutions of Ph_2MeP + RSH, CH_2=CMePh + RSH, and on a solution of CH_2=CMePh alone were also carried out. The progress of the reactions was regularly monitored by ^1H n.m.r. spectrometry. The relevant n.m.r. characteristics of both the reactants and products are listed in Table 6.

(iv) Photolysis of Tertiary and Ditertiary Phosphines in the presence of Thiols or Disulphides.

Equivalent concentrations (ca. 0.15 mol l^{-1}) of the phosphines, R^1_3P. (R^1_3=Ph_2Me, $Ph_2C_2H_4PPh_2$, $Ph_2CH_2PPh_2$, or $Ph_2CH_2P(S)Ph_2$), and either benzyl thiol or the disulphide, R_2S_2(R=Me or $PhCH_2$), were irradiated in deuteriobenzene solution in Pyrex n.m.r. tubes in a rigorous nitrogen atmosphere. Control experiments on the phosphines alone were also carried out. The progress of the reactions was regularly monitored by n.m.r. spectrometry. The results from these reactions are presented in Table 1 (p. 25 f). The relevant n.m.r. characteristics of both the reactants and products are listed in Table 2 (p.30).

TABLE 6. Selected n.m.r. characteristics used in the identification of the reactants and products in the photolysis of thiol-olefin-phosphine mixtures.[a]

Ph_2MeP	CH_3,1.37(d, $^2J_{PH}$ 3.9 Hz)
CH_2=CMePh	CH_3,1.97(m)[b]; CH_2,5.00,5.35(m)[b]
PhSH	SH,3.05(s)
^tBuSH	CH_3,1.20(s); SH,1.65(s)
$PhCH_2SH$	CH_2,3.33(d, $^3J_{HH}$ 8 Hz); SH,1.40(t, $^3J_{HH}$ 8 Hz)
Ph_2MePS	CH_3,1.77(d, $^2J_{PH}$ 13.2 Hz)
$PhSCH_2CHMePh$[c]	CH_3,1.20(d, $^3J_{HH}$ 6.8 Hz)
$^tBuSCH_2CHMePh$[c]	^{t}Bu,1.18(s); CH_3,1.10(?)[d]
$^tBuCH_2CHMePh$[c]	^{t}Bu,1.12(s); CH_3,1.10(?)[d]
$PhCH_2SCH_2CHMePh$[c]	$PhCH_2$,3.40(s); CH_3,1.20(d, $^3J_{HH}$ 6.8 Hz)
$PhCH_3$	CH_3,2.12(s)
^tBuH	CH_3,0.85(d, $^3J_{HH}$ 6 Hz)

[a] In C_6D_6. Proton chemical shifts (δ/p.p.m.) relative to internal $SiMe_4$. Only easily identifiable chemical shifts are listed. [b] Unresolved at 60 MHz. [c] The methylene protons are non-equivalent because of the adjacent asymmetric centre. The methylene resonance is further complicated because it overlaps with the methine signal. A complex multiplet in the region δ 2.4-3.0 results. [d] Tentative assignments due to overlap of all the methyl resonances.

(c) Photochemical Reactions between Tertiary Phosphines and Organic Diselenides.

Equivalent concentrations (ca. 0.18 mol l^{-1}) of the tertiary phosphine and organic diselenide in deuteriobenzene were irradiated in Pyrex n.m.r. tubes in a rigorous nitrogen atmosphere. Control experiments on solutions of R_2Se_2 alone were carried out simultaneously. The progress of the reactions was regularly monitored by n.m.r. spectrometry. The relevant n.m.r. characteristics of both the reactants and products are listed in Table 7. During irradiation the n.m.r. tubes were maintained at 285 K in a water-bath to avoid complicating thermal side reactions[25].

Similarly, equivalent concentrations of Ph_2Se_2 + CH_2=CMePh and Ph_2Se_2 + PhC≡CH in deuteriobenzene were irradiated in n.m.r. tubes for 40 h, but no change was detected by ^1H n.m.r. spectroscopy. Also, deuteriobenzene solutions of Me_2Se_2 + Ph_2Se_2 and Me_2Se_2 + Et_2Se_2 were irradiated for 20 h, but no mixed diselenides were observed. A reaction did occur, however, when a deuteriobenzene solution of Et_2Se_2 and Ph_2Se_2 was irradiated. The triplet due to the methyl protons of Et_2Se_2 (δ 1.22, $^3J_{HH}$ = 7 Hz) was joined by another triplet (δ 1.15, $^3J_{HH}$ = 7 Hz) after a brief period of irradiation (5 min). This latter triplet stopped growing in intensity after photolysis for ca. ½ h, an approximately 60:40 mixture of the upfield to downfield triplets having been produced. The quartet due to the methylene protons of Et_2Se_2 (δ 2.60, $^3J_{HH}$=7Hz) remained unchanged throughout the photolysis. A similar equilibrium mixture was also produced, however, when the two diselenides were allowed to stand in the dark for 4 h. The Ph_2Se_2/Et_2Se_2 mixture alone did not produce a deposit of elemental selenium

TABLE 7.

N.m.r. characteristics of the reactants and products involved in the photochemical reaction between tertiary phosphines and organic diselenides.

Compound	N.m.r. characteristics[a]	Literature Values (solvent)[b]
$(PhCH_2)_2Se_2$	Ph,7.10(s); CH_2,3.60(s)	Ph,6.91; CH_2,3.67(CD_3CN)[25]
Et_2Se_2	CH_3,1.22(t); CH_2,2.60(q)	CH_3,1.43; CH_2,2.86(None)[c]
Me_2Se_2	CH_3,2.17(s)	CH_3,2.55(None)[c]
Ph_2Se_2	o-Ph,7.52(m); m, p-Ph,6.92(m)	o-Ph,7.62; m, p-Ph,7.22 (CH_2Cl_2)[d]
$(PhCH_2)_2Se$	Ph,7.10(s); CH_2,3.47(s)	Ph,6.91; CH_2,3.55(CD_3CN)[25]
Et_2Se	CH_3,1.20(t); CH_2,2.30(q)	CH_3,1.37; CH_2,2.53(None)[c]
Me_2Se	CH_3,1.62(s)	CH_3,1.96(None)[c]
Ph_2Se	o-Ph,7.38(m)	o-Ph,7.45(None)[c]
Ph_2MeP	CH_3,1.37(d); $^2J_{PH}$3.9 Hz	CH_3,1.42; $^2J_{PH}$4.4 Hz(None)[e]
$PhMe_2P$	CH_3,1.07(d); $^2J_{PH}$3.3 Hz	CH_3,1.11; $^2J_{PH}$3.7 Hz (C_6H_6)[f]
Ph_2MePSe	CH_3,1.95(d); $^2J_{PH}$13.4 Hz ^{31}P, + 22.8	CH_3,2.33; $^2J_{PH}$13.2 Hz (CH_2Cl_2)[97] ^{31}P, + 22.3 (CH_2Cl_2)[97]
$PhMe_2PSe$	CH_3,1.58(d); $^2J_{PH}$13.4 Hz ^{31}P, + 14.8	CH_3,2.12; $^2J_{PH}$13.2 Hz (CH_2Cl_2)[97] ^{31}P, + 15.1 (CH_2Cl_2)[97]
Ph_3PSe	^{31}P, + 30.8	^{31}P, + 34.1 ($CDCl_3$)[97]

[a] In C_6D_6. Proton chemical shifts (δ, p.p.m.) relative to internal $SiMe_4$. Phosphorus chemical shifts are relative to external H_3PO_4.

[b] Values of chemical shifts may differ from our values due to a solute-deuterio-benzene shielding interaction; see e.g., R.S. Armstrong, M.J. Aroney, R.K. Duffin, H.J. Stootman, and R.J.W. Le Fevre, J.C.S. Perkin II, 1973, 1272. [c] M. Lardon, J. Amer. Chem. Soc., 1970, 92, 5063. [d] K.J. Wynne and P.S. Pearson, Inorg. Chem., 1972, 11, 1196. [e] H.H. Sisler and S.R. Jain, Inorg. Chem., 1968, 7, 104. [f] J.M. Jenkins and B.L. Shaw, J. Chem. Soc. (A), 1966, 770.

when the three diselenide mixtures were subjected to extended irradiation (20 h).

(d) Photochemical Reactions between Tertiary Phosphines and Organic Ditellurides.

Deuteriobenzene solutions of the ditellurides (ca. 0.14 mol l^{-1}), both alone and with one equivalent of tertiary phosphine added, were irradiated under nitrogen in inverted Pyrex n.m.r. tubes. These were kept immersed in a water bath at 285 K to avoid complicating thermal side reactions (which occurred when an analogous diselenide was photolysed without water-cooling[25]). The reactions were interrupted regularly (2 m intervals for $(PhCH_2)_2Te_2$ and 30 m intervals for Et_2Te_2) to monitor their progress by n.m.r. spectrometry and to remove deposited tellurium (which would ultimately have scattered all the u.v. radiation). Inversion of the tubes during irradiation ensured that the tellurium deposit did not affect the resolution of the spectra, and facilitated its removal (against a counter-current of N_2) since it adhered to the glass at the top of the tube.

Our attempts to isolate and fully characterise a sample of $(PhCH_2)_2Te$ from the photolysis of $(PhCH_2)_2Te_2$ failed. As the photolysis proceeded, the resonance at δ 3.95 (C_6D_6) due to the methylene protons of $(PhCH_2)_2Te_2$ diminished, and a signal at δ3.75, which we assign to $(PhCH_2)_2Te$, grew. Decomposition of this material to bibenzyl (δ 2.75) and tellurium began before the reaction was complete. A typical experiment on a larger scale (0.46 mmol of $(PhCH_2)_2Te_2$ in 25 ml of ether) produced $(PhCH_2)_2Te$ (58%) and bibenzyl (18%), with 24% unreacted starting material, after irradiation for 23 h. Attempts to isolate dibenzylmonotelluride from this mixture led to continued decomposiiton to bibenzyl and Te, even with only occasional exposures to diffuse day-

-light, suggesting that $(PhCH_2)_2Te$ might be thermally as well as photo-chemically sensitive.

CHAPTER 2

GROUP VI DERIVATIVES OF TERTIARY ARSINES

INTRODUCTION

Group VI Derivatives of Tertiary Arsines.

(a) Preparation of Tertiary Arsine Sulphides.

Sulphides of the type R_3AsS are usually prepared by the action of hydrogen sulphide on the oxides, dihydroxides, or dihalides (equation 61; X=Cl,Br,I,OH,½O).

$$R_3AsX_2 + H_2S \longrightarrow R_3AsS + 2HX \qquad (61)$$

For example, Jensen and Nielsen[56] prepared triphenylarsine sulphide by passing hydrogen sulphide through an ethanolic ammonia solution of triphenylarsine dibromide. They also stated that this compound could not be prepared directly from triphenylarsine and sulphur in carbon disulphide, even after prolonged refluxing.

Glidewell[57] synthesized Ph_3AsS by first oxidising Ph_3As with potassium permanganate in aqueous acetone to give $Ph_3AsO.H_2O$, which was then converted to Ph_3AsS by the action of hydrogen sulphide in ethanolic solution[58]. He also reported the high yield reaction of triphenylarsine with disulphur dichloride (equation 62).

$$Ph_3As + S_2Cl_2 \xrightarrow{1\ h,\ R.T.} Ph_3AsS + SCl_2 \qquad (62)$$

The arsine sulphide was also produced in the reaction of Ph_3As with sulphur dichloride, SCl_2 (equation 63).

$$Ph_3As + SCl_2 \longrightarrow Ph_3AsS + Cl_2 \qquad (63)$$

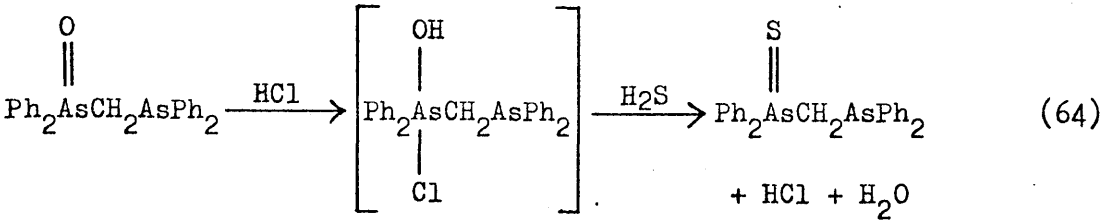
Zingaro and co-workers[59] prepared some tertiary alkyl arsine sulphides by refluxing an alcoholic solution of the arsine with sulphur. Tricyclohexylarsine sulphide, for example, was prepared in 89% yield after refluxing for thirty minutes. Methyldiphenylarsine sulphide, in contrast, could not be prepared even when the arsine was fused with sulphur. Vacuum distillation always led to the recovery of the unreacted arsine.

Reichle[60] described an unusual preparation of triphenylarsine sulphide from its corresponding oxide by refluxing Ph_3AsO in CS_2 (46 °C) for 1½ h. The arsine sulphide was produced in 85% yield, whereas the analogous reaction with Ph_3PO would not occur even in a high pressure stainless steel bomb at 250 °C.

Gatilov and Kamai[61] prepared some tertiary arsine sulphides by heating the arsine and sulphur in benzene at 100 °C for several hours. The extent of the reaction was determined by allowing the reaction mixture to cool, causing the precipitation of any unreacted sulphur. Ethylmethylphenylarsine sulphide, for instance, was obtained in 89% yield after heating at 100 °C for seven hours. They noted that as R in EtPhRAs changed from methyl, to ethyl, and so on up the homologous series, the number of hours required to cause complete reaction increased, and Ph_3AsS was obtained in 85% yield only after heating at 100 °C for forty hours.

The extent of the reaction of tertiary arsines with sulphur have been found to depend upon the reaction conditions as well as the groups attached to arsenic. The products were sometimes obtained in impure form because of the tendency for side-reactions to become more important as the reactivity of the arsine decreased. Chatt and Mann[62] discovered that the diarsine, 1,2-diphenylarsinoethane, $Ph_2AsC_2H_4AsPh_2$, did not combine with sulphur in boiling carbon disulphide solution. Tzschach and Lange[63], however, heated this diarsine with an excess of sulphur at 150 °C for 1 h and produced an almost quantitative yield of $Ph_2As(S)$-$C_2H_4As(S)Ph_2$. Lindner and Beer[64] used a sulphur-transfer agent, $PSCl_3$, to prepare this compound in 65% yield; the reaction required only stirring for 2 h at room temperature.

Cookson and Mann[65] prepared methylenebisdiphenylarsine monosulphide, $Ph_2As(S)CH_2AsPh_2$, by treating a hot chloroform solution of the corresponding monoxide, first with hydrogen chloride, and then with hydrogen sulphide (equation 64).



(64)

(b) Preparation of Tertiary Arsine Selenides.

Mel'nikov and Rokitskaya[66] reported that the reaction of triphenylarsine with selenium dioxide gave a mixture of Ph_3AsO and Ph_3AsSe. Zingaro and Merijanian[67], however, found no evidence for the formation of Ph_3AsSe in this reaction, nor from the fusion of the arsine with elemental selenium in a sealed tube at 225 °C nor from the reaction of triphenylarsine dihalides with hydrogen selenide. They did report that trialkylarsines undergo nucleophilic addition to elemental selenium in anhydrous alcohol or ether to give the trialkylarsine selenides in 40-70% yields. Zingaro[68] later claimed that triaryl arsine selenides had proved to be exceedingly elusive, and could not even be prepared by the reaction of KSeCN with the triaryl arsine. (The corresponding reaction with triaryl and alkyl-arylphosphines produced phosphine selenides of high purity in quantitative yield[69].) Jensen and Nielsen[56], however, isolated a mixture of the oxide and selenide of triphenylarsine from the reaction of triphenylarsine dichloride with hydrogen selenide at 0 °C. A reasonably pure sample of Ph_3AsSe was obtained by recrystallization of the mixture from aqueous ethanol (without heating as the arsine selenide was heat sensitive).

Recently, Glidewell[57] studied the reaction of selenium dioxide with Ph_3M (M=N,P,As,Sb,Bi); no reaction occurred when M=N or Bi and

when M=P or Sb the sole products, apart from red selenium, were Ph_3PO and $Ph_3Sb(OH)_2$, respectively. There was some evidence, however, for the transient formation of Ph_3AsSe; a colourless oil was obtained from the reaction, which rapidly (< 1 min) solidified, depositing red selenium in great amounts. Extraction of the solid with hot benzene yielded only Ph_3As, but it was thought likely that the oil was indeed the thermodynamically unstable triphenylarsine selenide.

Krishnan et al.,[70] in a study of the products formed in the reaction between triphenylarsine and SeS_2, obtained a solid 1:1 mixture of Ph_3AsS and Ph_3AsSe. Infrared, X-ray and microanalytical investigations on the product suggested that it should be formulated as a solid solution (mixed crystal) of $Ph_3AsS.Ph_3AsSe$. Attempts to separate the two components by reacting the adduct with $HgCl_2$, resulted only in the formation of the complex $(Ph_3AsS)_2HgCl_2$ and the precipitation of black selenium. The instability of Ph_3AsSe in solution once more became obvious.

A successful demonstration of the existence of R_3AsTe has not yet been reported.

(c) Adducts of Tertiary Phosphine and Arsine Chalcogenides.

Tertiary phosphine oxides, sulphides, and selenides form stable adducts with halogens and interhalogens. The stability of these charge-transfer complexes with iodine, for example, follow the order, P=Se > P=S > P=O. A possible explanation in terms of simple molecular orbital theory was proposed by Bruno and co-workers[71], who in a study of the equilibrium constants for the formation of charge transfer complexes between iodine and the tris(dimethylamino)phosphine chalcogenides, $(Me_2N)_3PX$ (X=O,S,Se), suggested that the back donation of $p\pi$ halogen

electrons to the 3d and 4d orbitals of S or Se, respectively, would strengthen the $X \rightarrow I_2$ interaction for S and Se, but could not for O. It was also thought reasonable that the 5p level on iodine would mix better with the 4d level on Se, because of the greater proximity of their energies, rather than with the 3d level on S which is much lower in energy. Kolar, Zingaro and Irgolic[72] have discovered that trialkylphosphine and trialkylarsine chalcogenides are stronger donors towards the halogens than the corresponding triphenyl derivatives. This was to be expected because of the greater electron-releasing ability of the alkyl groups. The nature of the organic substituent, however, was thought to be not as critical as the chalcogen atom or the Group VA atom in determining the stability of the complex. They suggested that among R_3MX molecules (M=P,As;X=O,S,Se) the donor strength would increase as the electronegativity of M decreased. This was because the electron density around the σ-donor atom, X, was expected to decrease upon complexation with the iodine acceptor. The greater the electronegativity of M, the less would be the tendency of X to function as a σ-donor. Thus, they rationalized their finding that R_3AsO molecules are considerably stronger donors than the corresponding R_3PO molecules.

Similarly, Gallagher, Graddon and Sheikh[73] found that tertiary arsine sulphides were stronger bases than the corresponding phosphine sulphides, forming more stable adducts with the mercury (II) halides. The difference in base strength was considered to be a result of the greater electron withdrawal from the donor sulphur atoms by the more electronegative phosphorus atoms. This difference was represented as a greater contribution of the resonance structure (III) compared with (IV) for the phosphine sulphides.

$$Ph_3M{=}S \longleftrightarrow Ph_3\overset{+}{M}{-}\overset{-}{S}$$

(III) (IV)

Zingaro and Meyers[74] examined the ultraviolet absorption spectra of mixtures of iodine and arsine sulphides in chloroform. Their results suggested the presence of the triiodide ion, I_3^-, and they concluded that the arsine sulphides reacted irreversibly with iodine with rupture of the As-S bond and formed trialkyl-(or aryl-)triiodides, $[R_3AsI]^+I_3^-$.

Vetter discovered in 1964[75] that hexamethylphosphoramide (HMPA) forms 1:1 adducts with $POCl_3$ and $POBr_3$, the i.r. spectra of which indicated that the P atom of the phosphoryl halide acted as the electrophilic centre, accepting electron density from the oxygen of HMPA.

Murch[76] has capitalized on this discovery in that treatment of 1 mole of HMPA with 1 mole of $POCl_3$ in benzene produced the adduct, $(Me_2N)_3PO.POCl_3$, which when treated with alcohols gave a compound with the formula $(Me_2N)_3PO.(RO)_3PO$, useful as a fire-retardant for polyesters.

RESULTS AND DISCUSSION

(A) Attempted syntheses of tertiary arsine sulphides.

In order to continue our study of sulphur and selenium exchange processes, which were found to take place between tertiary phosphine chalcogenides and tertiary phosphines (see Chapter 3), it was necessary that some tertiary arsine sulphides be synthesized (and, if possible, the analogous arsine selenides).

A number of possible synthetic routes were tried and these will be considered individually.

(i) Reaction of Ph_2RAs with sulphur.

The reaction between Ph_2RAs(R=Me,Ph,CH_2AsPh_2,$C_2H_4AsPh_2$) and sulphur in solution was studied. For R=Me, no reaction occurred in benzene after heating at 80 °C for 20 h. Chivers and Drummond[77] reported, in a short communication, that hexamethylphosphoramide (HMPA), $(Me_2N)_3PO$, was a useful catalyst for preparative reactions involving elemental sulphur, since sulphur readily dissolved in anhydrous HMPA at 25 °C. They found, for example, that the phosphine sulphides Ph_3PS, $Ph_2P(S)C_2H_4P(S)Ph_2$ and $(C_6H_{11})_3PS$ could readily be prepared in good yields at room temperature (without HMPA moderate warming or refluxing was necessary to cause the reaction to go to completion[78]) by addition of the appropriate phosphine to a solution of sulphur in carbon disulphide/HMPA (70:30;v/v).

A 1:1 mixture of Ph_2MeAs and sulphur in benzene/HMPA (80:20;v/v) was, therefore, stirred for 20 h at room temperature. A ^1H n.m.r. spectrum of an aliquot indicated that some arsine remained, but the strong doublet, due to the eighteen equivalent methyl protons (coupled to ^{31}P) of HMPA obscured the region where the methyl protons of Ph_2MeAsS were expected to appear. After removing most of the HMPA by extracting it into the water layer of a benzene-water mixture, and on removing most

of the benzene and adding n-pentane, clear, colourless, crystals formed, the n.m.r. spectrum of which indicated a 1:1 mixture of Ph_2MeAsS and HMPA. Microanalysis confirmed that an adduct of composition Ph_2MeAsS.HMPA had been produced. The yield, however, was only approximately 30%, some 60-70% of unreacted arsine being recovered.

The reaction of this arsine with sulphur is obviously slow at 80 °C in benzene and at room temperature in the presence of HMPA. It was, therefore, attempted at temperatures between 135° and 145° in o-dichlorobenzene and after 24 h a 4:1 mixture of the arsine sulphide and arsine had been produced. Heating for another 6 h at these temperatures caused little further reaction. On removing the volatiles a dark brown oil remained which repeatedly failed to crystallize from a variety of solvent mixtures. The arsine sulphide, on addition of some HMPA, and after seeding with crystal fragments of the Ph_2MeAsS.HMPA adduct, finally crystallised as the adduct in 71% yield.

Triphenylarsine sulphide was similarly produced in 60% yield after heating for 8 h at 150 °C in o-dichlorobenzene. Bis(diphenylarsino)methane, $Ph_2AsCH_2AsPh_2$, was recovered unchanged after refluxing with sulphur in toluene for 24 h. When, however, the diarsine was heated with an excess of sulphur at 150 °C for 14 h in o-dichlorobenzene, only the diarsine monosulphide, $Ph_2As(S)CH_2AsPh_2$, was isolated (as determined by microanalysis and ^1H n.m.r. and i.r. spectroscopy) in 70% yield. No further reaction of the monosulphide to the disulphide $Ph_2As(S)CH_2As(S)Ph_2$ apparently occurs under these reaction conditions.* This may be attributed to the process of inductive deactivation whereby the inductive effect of the slightly positive As(V) atom in the monosulphide reduces the basicity and hence reactivity of the other As(III) atom. A similar effect is observed with the analogous diphosphine monosulphide, $Ph_2P(S)$-

* The synthesis of the disulphide by heating the diarsine and sulphur in xylene was recently reported, but gave anomalous results in a metal-ligand bond formation study.[73]

CH_2PPh_2, although in this case the disulphide is readily produced by the reaction of the diphosphine with an excess of sulphur. Thus, on heating an equimolar mixture of the diphosphine disulphide and the diphosphine at 160 °C for 24 h, $Ph_2P(S)CH_2PPh_2$, the thermodynamically more stable phosphine sulphide, is produced quantitatively.[79]

A neat mixture of 1,2-bis(diphenylarsino)ethane, $Ph_2AsC_2H_4AsPh_2$, and an excess of sulphur was heated at 150 °C until the mixture solidified[63], but several recrystallisations, necessary to remove the unreacted sulphur, reduced the yield to only 40%.

(ii) Reaction between Ph_2RAs and disulphur dichloride.

The syntheses of some tertiary arsine sulphides using the method disclosed by Glidewell[57] were attempted, but in all three cases the arsine reacted with S_2Cl_2 to produce the arsine dichloride instead of the arsine sulphide (equation 65; R=Ph,Me, and $CH_2As(S)Ph_2$).

$$Ph_2RAs + S_2Cl_2 \xrightarrow[R.T.]{ether} Ph_2RAsCl_2 + \tfrac{1}{4}S_8 \qquad (65)$$

Kustan and co-workers[80] have reported that triaryl phosphines react with SCl_2 to give triarylphosphine dichloride and sulphur and/or triarylphosphine sulphide depending on the mole ratio of the reactants. Thus, reaction of an equimolar mixture of Ph_3P and SCl_2 resulted in the formation of the phosphine dichloride (isolated as Ph_3PO by hydrolysis) and sulphur, whereas, with a twofold excess of the phosphine, approximately equal amounts of Ph_3PCl_2 and Ph_3PS were produced (equations 66 and 67; R=Ph, M=P).

$$R_3M + SCl_2 \longrightarrow R_3MCl_2 + S \qquad (66)$$

$$2R_3M + SCl_2 \longrightarrow R_3MCl_2 + R_3MS \qquad (67)$$

They also found that the reaction between equimolar amounts of Ph_3As and

SCl_2 produced Ph_3AsCl_2 and sulphur, contrary to the more recent report by Glidewell[57] (equation 63). With a twofold excess of arsine, reaction 67 (R=Ph, M=As) apparently occurred although no experimental details of this reaction were provided. The triaryl-phosphines and -arsine reacted faster with SCl_2 than with sulphur and therefore no phosphine- or arsine-sulphides were produced in reaction 66, but they were produced in reaction 67 because the excess phosphine or arsine reacted with the sulphur that had been formed in the reaction with the first mole of phosphine or arsine (equation 66).

The experimental procedure used by Kustan[80] simply involved the slow addition of a benzene solution of SCl_2 to a stirred solution of the triarylpnictogen R_3M(M=P,As,Sb) in benzene at 10 °C. Reaction occurred immediately and the mixtures were allowed to warm to room temperature.

Glidewell's procedure[57] either involved the dropwise addition of S_2Cl_2 or SCl_2 to an ether solution of the triphenylpnictogen Ph_3M(M=N,P, As,Sb,Bi), or the mixing of equimolar quantities of the reactants in ether. Stirring for 1 h at room temperature resulted in the formation of the products as shown in equations 62 and 63.

Our procedure involved firstly the vacuum transfer of S_2Cl_2 into an ether solution of the arsine at -196 °C, which on warming to room temperature resulted in immediate reaction precipitating a yellow solid, which, after extraction with chloroform (to remove the elemental sulphur), proved to be the arsine dichloride (as determined by ^1H n.m.r. and i.r. spectroscopy). Secondly, the procedure used by Glidewell[57] was followed as closely as possible, although an ether solution of S_2Cl_2 was added dropwise rather than S_2Cl_2 alone. Once again, however, the arsine dichloride and sulphur were produced.

Glidewell[57] noted that for the equilibrium (68) the ΔH° term

strongly favoured triphenylpnictogen dichloride and elemental sulphur.

$$Ph_3MS + SCl_2 \rightleftharpoons Ph_3MCl_2 + \tfrac{1}{4}S_8 \qquad (68)$$

He therefore stated that any rationalisation of his observed products must be in mechanistic terms. Kustan's work[80] suggested that the favoured reaction would depend upon changes in the relative stabilities of the sulphides and dichlorides of the triaryl derivatives of Group V. A good explanation of these apparently conflicting results is not immediately obvious, although the fact that for M=Sb and Bi, only the dichlorides were formed in the reaction of the triphenyl derivatives with both S_2Cl_2 and SCl_2[57], may favour the rationalisation in terms of the relative stabilities of the pnictogen dichlorides and sulphides. For example, Ph_3SbCl_2 is stable in air, whereas Ph_3Sb does not react with sulphur under any of the above conditions[80] and Ph_3SbS has only been prepared by the reaction of Ph_3SbCl_2 with hydrogen sulphide[81].

(iii) Reaction of R_3AsCl_2 and hydrogen sulphide.

Diphenylmethylarsine dichloride, $Ph_2MeAsCl_2$, prepared as outlined in section (ii), was dissolved in ethanol and hydrogen sulphide was bubbled into the solution for 1 h. After removal of the volatiles a viscous green-tinted liquid remained, the ^1H n.m.r. spectrum of which showed that Ph_2MeAsS had indeed been produced in good yield. Again, however, all attempts to recrystallise the sulphide failed, and it was finally concluded that it must be an oil which would only crystallise at room temperature in the presence of HMPA as a 1:1 adduct.

An attempt was made, therefore, to purify this arsine sulphide by vacuum distillation using a cold finger with an attached cup in which the condensed product would collect. The oil was heated under vacuum (0.06 mm) at 120 °C for a few hours, but the initially slightly yellow liquid which collected rapidly turned deep-brown in colour; the ^1H n.m.r.

spectrum of the product was found to be a mixture of Ph_2MeAsS and Ph_2-MeAs (ca. 5:1, respectively), indicating that the arsine sulphide is thermally unstable and decomposes to the arsine and sulphur under these conditions.

(iv) Sulphur exchange reaction between Ph_3AsS and Ph_2MeAs.

Triphenylarsine sulphide is a readily prepared and isolated white solid (see p. 68) and, because Ph_2MeAs was thought to be the more basic arsine, the sulphur exchange reaction (equation 69) was attempted, since it was discovered that Ph_3As could be sublimed from a Ph_3AsS/Ph_3As mixture under vacuum, and this might allow the isolation of a pure sample of Ph_2MeAsS.

$$Ph_3AsS + Ph_2MeAs \rightleftharpoons Ph_3As + Ph_2MeAsS \qquad (69)$$

A 1:1 mixture of Ph_3AsS and Ph_2MeAs was dissolved in deuteriochloroform in a n.m.r. tube, and after standing at room temperature overnight (19 h), an equilibrium mixture of all four components existed, the equilibrium lying more to the right-hand side of equation 69 (approx. 70:30 mixture of Ph_2MeAsS and Ph_2MeAs, respectively, as determined by integration of their respective methyl protons). An excess of Ph_3AsS was added to try to push the equilibrium even further over to the right, but after the addition of half of an equivalent, it became clear that the mixture would not go much beyond a 85:15 mixture of Ph_2MeAsS and Ph_2MeAs, respectively. This equilibrium mixture was, therefore heated for 5-6 h in a sublimation unit under vacuum (0.06 mm) at temperatures up to 82 °C [Ph_3As was known to sublime under these conditions and it was essential that the arsine sulphide, Ph_2MeAsS, should not be heated too strongly (see p. 71)]. However, a colourless viscous liquid condensed on the cold finger (Ph_3-As is a white solid) and a ^1H n.m.r. spectrum of the residue was found to consist almost entirely of Ph_3AsS with only traces of Ph_2MeAsS and

Ph_3As. The condensed liquid was obviously Ph_2MeAs, which, being the most volatile component, condensed out of the mixture pulling equilibrium 69 back over to the left-hand side and making the isolation of a pure sample of Ph_2MeAsS impossible by this means.

Thus the isolation of a pure sample of diphenylmethylarsine sulphide was found to be impossible although it could be obtained as a crude oil or as a crystalline adduct with HMPA. The thermal instability of Ph_2MeAsS at temperatures above 100 °C may explain why Zingaro and coworkers[59] always failed to isolate this arsine sulphide from the fusion of the arsine and sulphur at elevated temperatures followed by vacuum distillation of the products.

No arsine selenides were prepared owing to the difficulties experienced in isolating the analogous arsine sulphides and the reported instability of all but the trialkylarsine selenides[68]. An equimolar mixture of diphenylmethylarsine and powdered black selenium was heated in deuteriobenzene in a n.m.r. tube at 80 °C for 20 h, but only a broadening of the signal due to the methyl protons of the arsine was observed (as well as a 2 Hz shift downfield). The spectrum remained the same even when the solution was decanted into a fresh n.m.r. tube to remove the selenium powder. This may indicate that a fast exchange of selenium occurs between the arsine selenide and the arsine (analogous to the fast exchange of tellurium between R_3PTe and R_3P molecules described in Chapter 1, p.48), precluding the isolation of the former (equations 70 and/or 71; R_3=Ph_2Me).

$$R_3AsSe \rightleftharpoons R_3As + Se \qquad (70)$$

$$R_3AsSe + R_3As \rightleftharpoons R_3As + R_3AsSe \qquad (71)$$

A similar result was obtained with $Ph_2AsC_2H_4AsPh_2$, only a broadening of the signal due to the methylene protons of the diarsine being observed.

(B) Adducts of Tertiary Phosphine and Arsine Chalcogenides.

Our discovery that diphenylmethylarsine sulphide forms a crystalline adduct with hexamethylphosphoramide (HMPA), when a poor solvent like pentane is added to a concentrated solution of the two compounds in benzene (as described in section A, p. 68), stimulated our interest in this little studied area of phosphorus-arsenic chemistry.

As described in the introduction there were only two previous reports in the literature of 1:1 adducts between firstly, $POCl_3$ or $POBr_3$ and HMPA[75], and secondly, $(RO)_3PO$ and HMPA[76].

Binder and Fluck[82], however, formulated the former adduct as a phosphonium salt, $\left[(Me_2N)_3\overset{+}{P}\text{-O-}POCl_2\right]Cl^-$, due to the observation of two ^{31}P chemical shifts not attributable to the individual components.

We attempted to isolate a 1:1 adduct of triphenylphosphine sulphide and trimethyl phosphate to determine whether this phenomenon was general to any combination of Group V chalcogenides. Ph_3PS was dissolved in a 2:1 mixture of benzene and $(MeO)_3PO$, respectively, and left to recrystallise slowly on evaporation of the benzene. After a short while, clear, colourless needles began to form. These were filtered, washed with a small amount of benzene, and then dried under vacuum (0.06 mm) at room temperature for 3 h. A ^1H n.m.r. spectrum of the crystals showed, however, that no adduct had been formed, only Ph_3PS being present. Similarly, when Ph_3AsS was recrystallised from a benzene/HMPA solvent mixture, the arsine sulphide alone was isolated as a white solid.

During this work, Krishnan and co-workers[70] reported the isolation of 1:1 adducts between Ph_3PS and Ph_3PSe and between Ph_3AsS and Ph_3AsSe. These were obtained from the reaction of the respective phosphine or arsine with SeS_2 (equation 72; M=P or As).

$$Ph_3M + SeS_2 \longrightarrow Ph_3MS.Ph_3MSe \qquad (72)$$

The products obtained in these reactions were formulated either as a solid solution (mixed crystal) of $Ph_3MS.Ph_3MSe$ or as a selenosulphide, $Ph_3MSe\text{-}SMPh_3$. The appearance of strong i.r. absorption bands in the product mixtures typical of the individual components led them to suggest that the adduct was a solid solution and not a selenosulphide, since the latter's formation would have resulted in a lowering of the respective ν(M=S) and ν(M=Se) frequencies. Also, a single-crystal X-ray investigation of the adducts revealed that they were isomorphous with the individual phosphine and arsine sulphides.

Correlations between the stretching frequency of the M-X bond in R_3MX molecules (M=P,As; X=O,S) and the electronegativities of the substituent groups R_3, have indicated that electronegative substituents increase the strength of this bond by making M more positive and therefore increasing the ($\underline{p}\rightarrow\underline{d}$) π- interaction from X to M. Zingaro has shown, for example, that the electronegativity of the substituents on the phosphorus atom in tertiary phosphine sulphides[83], and on the arsenic atom in tertiary arsine sulphides[59], plays an important role in determining the frequency of the fundamental P=S and As=S vibrations.

Table 8 lists the i.r. stretching frequencies of the M=X bonds in certain R_3MX molecules (M=P,X=O,S and M=As,X=S). The effect of the electronegativity of the substituents on phosphorus or arsenic can be seen by comparing the triphenyl derivatives with the trimethyl derivatives in Table 8. The greater the substituent's electronegativity (Ph > Me), the more positive the P or As atom becomes; the bond order increases by increased ($\underline{p}\rightarrow\underline{d}$) π-bonding from the filled $\underline{p}$-orbitals on sulphur (or oxygen) to the empty $\underline{d}$-orbitals on phosphorus or arsenic.

The position of the M=X stretching frequency can therefore give

TABLE 8. ν(M=X) in R_3MX Molecules.

	Literature Values		This Work
R_3MX	ν(M=X) (cm^{-1}) (Solid State)	ν(M=X) (cm^{-1}) (Solution)	ν(M=X) (cm^{-1}) (Phase)
Me_3PO	1174 (KBr)[a]	-	-
Ph_3PO	1190 (Nujol)[b]	1201 (CS_2)[b]	-
$(Me_2N)_3PO$	-	1215 (CCl_4)[c]	-
	-	1208 (Film)[d]	1209 (Film)
$(MeO)_3PO$	-	1277 (CCl_4)[e]	-
Cl_3PO	-	1301 (CCl_4)[e]	-
	-	1300 (Film)	-
Me_3PS	570 (KBr)[83]	566 (Hexane)[g]	-
$(Me_2N)_3PS$	567 (Nujol)[h]	560 (Hexane)[g]	-
$(MeO)_3PS$	-	618 (Film)[i]	-
Ph_3PS	634 (Nujol)[b]	642 (CS_2)[b]	638 (KBr)
Cl_3PS	-	752 (Film)[j]	-
Me_3AsS	473 (KBr)[59]	473 ($CHCl_3$)[59]	-
Ph_2MeAsS	-	-	491,480(Film)
Ph_3AsS	495 (KBr)[56]	-	497 (KBr)

TABLE 8 Contd.

R_3MX	Literature Values $\nu(M{=}X)$ (cm^{-1}) (Solid State)	Literature Values $\nu(M{=}X)$ (cm^{-1}) (Solution)	This Work $\nu(M{=}X)$ (cm^{-1}) (Phase)
Ph_2MeAsS. $(Me_2N)_3PO$ (Adduct)			496,483; 1198 (KBr)

[a] F.A. Cotton, R.D. Barner, and E. Bannister, J. Chem. Soc., 1960, 2199. [b] R.F. De Ketelaere and G.P. Van der Kelen, J. Mol. Struct., 1974, 23, 233. [c] H. Schulze and A. Mueller, Z. Naturforsch, 1970, 25B, 148. [d] J.T. Donoghue and R.S. Drago, Inorg. Chem., 1963, 2, 1158. [e] H. Goldwhite and J. Previdi, Spectrochim. Acta, 1970, 26A, 1403. [f] J.C. Sheldon and S.Y. Tyree, J. Amer. Chem. Soc., 1958, 80, 4775. [g] P.M. Boorman, S.A. Clow, D. Potts, and H. Wieser, Inorg. Nuc. Chem. Letters, 1973, 9, 941. [h] J. Kincaid, K. Nakamoto, J.A. Tiethof and D.W. Meek, Spectrochim. Acta, 1974, 30A, 2091. [i] J.R. Durig and J.S. Diyorio, J. Mol. Struct., 1969, 3, 179. [j] J.R. Durig and J.W. Clark, J. Chem. Phys. 1967, 46, 3057.

a qualitative estimate of the relative amounts of π-bonding in related R_3MX molecules, and indicate whether the bonding in the chalcogenide is better described as either $R_3M{=}X$ or $R_3\overset{+}{M}\text{-}\overset{-}{X}$. The smaller the M=X frequency for a particular MX in a series of R_3MX compounds, the better the compound will be as a donor molecule towards other electron-acceptor molecules (Donor strength or basicity is proportional to the M-X bond polarity.) The trimethyl derivatives of the three groups of R_3MX molecules in Table 8 should therefore be better electron donors than, for example, their corresponding triphenyl derivatives, since the bonding in the former is better described as $Me_3\overset{+}{M}\text{-}\overset{-}{X}$ rather than $Me_3M{=}X$, the triphenyl derivatives having relatively more double-bond character in the M-X bond than the trimethyl derivatives. Thus, the trimethyl derivatives should more readily form crystalline adducts with other electron-accepting molecules.

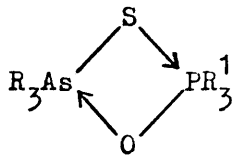
Using this relationship between ν(M=X) and bond polarity might allow i.r. frequencies to be used in determining the relative donor or acceptor potential of R_3MX in donor/acceptor complexes between two such molecules (since a poor donor might well be a good acceptor). Thus, by considering the position of the P=O band in HMPA, relative to the bands for the other R_3PO molecules (Table 8), it would appear that it should be a good donor molecule (although probably not as good as Me_3PO or Ph_3PO), and should form adducts with good electron-accepting molecules; Cl_3PO, for example. This might explain Vetter's isolation of a 1:1 adduct between $POCl_3$ and HMPA[75], and Murch's 1:1 adduct between $(EtO)_3PO$ and HMPA[76] [triethyl phosphate has a P=O band at about 1270 cm^{-1} (CCl_4)[84]]. Also, our failure to isolate an adduct from a solution of Ph_3PS and $(MeO)_3PO$ might be accounted for, because the former is not a particularly good electron donor [both $(Me_2N)_3PS$ and $(MeO)_3PS$ have lower P=S frequencies in contrast to the position of Ph_3PO in the R_3PO series (Table 8)].

Comparisons of the relative donor or acceptor properties between different series of R_3MX molecules seem even more tentative than those within one series. Carlson and Meek[1], from a study of the dipole moments of thirteen phosphine and two arsine chalcogenides, and from previous dipole moment studies, concluded that the arsine compounds R_3MX (M=As, R=Ph or Me, and X=O or S) were more polar than the corresponding phosphine compounds. The polarity of the phosphine derivatives was observed to increase in the order oxide < sulphide < selenide, and electronegative groups decreased the polarity of the derivative. Their results were consistent with previous chemical and physical studies on the donor properties, bond orders, and bond energies of the M-X bond, which all showed that there was greater double-bond character in the phosphorus-oxygen bond than in the phosphorus-sulphur bond.[1]

The order of increasing donor strength, with respect to the R_3MX molecules listed in Table 8, would, therefore, appear to be R_3PO < R_3PS < R_3AsS.

A negative shift of the M=X stretching vibration frequency of R_3MX molecules is invariably observed when such molecules form complexes with transition metals[85]. This was thought to be due to a reduction in the amount of ($\underline{p}\rightarrow\underline{d}$) π-bonding from X$\longrightarrow$M because of the movement of electrons from X to the metal upon complex formation[86]. Vetter[75], similarly, noted a reduction (35 cm^{-1}) in the P=O frequency of HMPA in its 1:1 adduct with Cl_3PO and concluded that the oxygen atom of HMPA must be the nucleophilic centre coordinating to the phosphorus of $POCl_3$. A comparison of the P=O and As=S stretching frequencies of the Ph_2MeAsS. HMPA adduct with the frequencies of the individual components (Table 8), however, shows that the P=O frequency has been reduced by <u>ca.</u> 11 cm^{-1} in the adduct, whereas the As=S frequency has increased by <u>ca.</u> 5 cm^{-1}.

These frequency shifts may be partly due to the different phases used to record the i.r. spectra of the adduct (KBr disc) and the individual components of the adduct (thin films). Nevertheless it is still probable that there is a weak interaction between the two components enabling them to orientate in such a way so as to crystallise as a 1:1 adduct. It would appear, though, that HMPA is acting as the electron donor (as it also appears to do in the $POCl_3$.HMPA adduct[75]), since a reduction in its P=O frequency in the adduct is consistent with electron density being removed from the P=O bond. The corresponding increase in the As=S stretching frequency seems to support this idea, although the relative frequency shifts may be due to a mass effect resulting from the formation of a four-membered ring, as depicted in structure V (R=Ph_2Me, R^1=Me_2N).



Structure V

Therefore, from a consideration of the relative donor strengths of Ph_2MeAsS and HMPA, the former would have been predicted to be the donor in the 1:1 adduct formed between them. The frequency shift results, in contrast, suggest that HMPA is acting as the donor molecule. More light will be shed on the nature of the bonding upon completion of a proposed X-ray crystallographic study of this adduct.

It thus appears to be quite difficult to rationalize the probability of adduct formation between phosphine oxides and arsine sulphides in general, since, as the above example illustrates, it may not be clear which component will act as the electron donor in a particular case. Our inability to isolate the very similar adduct, Ph_3AsS.HMPA, may suggest that the formation of an adduct between Ph_2MeAsS and HMPA is due to other characteristics peculiar to this combination of molecules.

Experimental.

The spectroscopic instrumentation used was as described in the experimental section of Chapter 1 (p.52). Melting points (uncorrected) were obtained on a Reichert-Kofler hot-stage apparatus.

The various tertiary arsines used in this work were obtained commercially either from Strem Chemicals Inc., or Fluorochem Ltd. Hexamethylphosphoramide, trimethyl phosphate and sulphur monochloride were all supplied by BDH Chemicals Ltd. The Aldrich Chemical Co., Ltd., supplied o-dichlorobenzene, and deuterated benzene and chloroform were obtained commercially from CEA-France. The purity of all the commercial products was at least 97% and in most cases $\geq$ 99%. They were all used without further purification (except S_2Cl_2, which was distilled prior to use), their purity being further confirmed by the absence of spurious peaks in their n.m.r. spectra. Triphenylphosphine sulphide was prepared by the reaction of Ph_3P and sulphur in refluxing benzene solution.

Table 9 lists some selected n.m.r. characteristics of the tertiary arsines and their Group VI derivatives studied in this work.

Table 9

Selected n.m.r. characteristics of tertiary arsine derivatives.

Compound	N.m.r. characteristics[a]
$Ph_2AsCH_2AsPh_2$	CH_2,2.61(s)
$Ph_2AsCH_2As(S)Ph_2$	CH_2,3.15(s)
$Ph_2AsC_2H_4AsPh_2$	CH_2,2.13(s)
$Ph_2AsC_2H_4As(S)Ph_2$	CH_2,2.43(m)
$Ph_2As(S)C_2H_4As(S)Ph_2$	CH_2,2.80(s)
Ph_2MeAs	CH_3,1.47(s)
Ph_2MeAs	CH_3,1.25(s)[b]
Ph_2MeAsS	CH_3,2.20(s); o-Ph,7.82(m); m,p-Ph,7.55(m)
Ph_2MeAsS	CH_3,1.65(s); o-Ph,7.75(m); m,p-Ph,7.05(m)[b]
$(Me_2N)_3PO$(HMPA)	CH_3,2.65(d); $^3J_{PH}$ 9.5 Hz
$(Me_2N)_3PO$(HMPA)	CH_3,2.45(d); $^3J_{PH}$ 9.5 Hz[b]
Ph_3As	Ph, 7.35(s)
Ph_3AsS	o-Ph,7.80(m); m,p-Ph,7.55
$Ph_2MeAsCl_2$	CH_3,3.45(s); o-Ph,8.08(m); m,p-Ph,7.60(m)

[a] In $CDCl_3$ unless otherwise stated. Proton chemical shifts (δ/p.p.m.) relative to internal $SiMe_4$. (s) = singlet, (d) = doublet, and (m) = multiplet. [b] In C_6D_6. Note upfield chemical shift displacement due to solute-deuteriobenzene interaction, as described in J.C.S. Perkin II, 1973, 1272, by R.S. Armstrong et al.

(A) Attempted syntheses of some tertiary arsine sulphides.

(i) Reaction of tertiary arsines with elemental sulphur.

Ph_2MeAs + sulphur in deuteriobenzene.

Sulphur (3.4 mg, 0.106 mmol) was placed in a n.m.r. tube which had been flushed out with dry nitrogen. Ph_2MeAs (20 µl, 0.104 mmol) was then added against a counter-current of N_2 (using a 10 µl syringe), followed by deuteriobenzene (ca. 0.3 ml). The n.m.r. tube mixture was heated in an oil bath at 80 °C for 20 h, the progress of the reaction being monitored periodically by ^1H n.m.r. spectrometry. No new signals were observed indicating either a very slow reaction or no reaction at all.

Ph_2MeAs + sulphur + hexamethylphosphoramide (HMPA).

Sulphur (83.5 mg, 2.61 mmol) was placed in a three-necked r.b. flask (100 ml) which had been flushed out with dry nitrogen for 1 h. A solvent mixture consisting of benzene (20 ml) and HMPA (5 ml) was added, and after stirring for a few minutes the sulphur dissolved. Ph_2MeAs (0.5 ml, 2.6 mmol) was added using a glass syringe (2 ml) and the resulting clear, colourless solution was stirred at room temperature for a total of 20 h. An aliquot was removed at this stage to determine the extent of the reaction. The ^1H n.m.r. showed the presence of unreacted Ph_2MeAs (Table 9), but the strong methyl doublet of HMPA (Table) obscured the region in the spectrum where the peak due to the methyl protons of Ph_2MeAsS was expected to occur. The products were therefore extracted with a benzene-water mixture, most of the HMPA going into the water layer. The benzene layer was dried over anhydrous $MgSO_4$, then reduced in volume prior to the addition of a small amount of n-pentane. Clear, colourless crystals separated out, (contaminated slightly with sulphur) which when recrystallised from cyclohexane gave a total yield of 0.4 g of crystalline product. Analysis by ^1H n.m.r. and i.r. spectrometry

showed that the product was a mixture of Ph_2MeAsS and HMPA (see Table 8, p.76, for the As=S and P=O i.r. stretching frequencies, and Table 9 for the n.m.r. parameters of the dissolved solid mixture). Integration of the ^1H n.m.r. spectrum revealed that an almost exactly 1:1 mixture of these two components had crystallised. The recrystallised yield of the adduct was 29.8% with respect to the amount of arsine sulphide in the $Ph_2MeAsS.HMPA$ adduct relative to the amount of arsine used. Microanalysis confirmed the 1:1 ratio of HMPA to Ph_2MeAsS. (Found: C, 50.21; H, 6.90; N, 9.12%. Calc. for $C_{19}H_{31}AsN_3OPS$ ($C_{13}H_{13}AsS.\ C_6H_{18}N_3OP$): C, 50.09; H, 6.86; N, 9.23%; M, 455.)

Ph_2MeAs + sulphur in o-dichlorobenzene.

Sulphur (0.2 g, 6.25 mmol.) was placed in a three-necked r.b. flask (100 ml) fitted with a reflux condenser and a N_2 inlet/outlet system. The vessel was purged with dry N_2 prior to the addition of o-dichlorobenzene (20 ml) and Ph_2MeAs (1 ml, 5.2 mmol). The mixture was heated in an oil-bath at temperatures between 135 °C and 145 °C for a total of 24 h (the sulphur dissolved when the temperature reached 130 °C). Removal of an aliquot of the reaction mixture at this stage for ^1H n.m.r. monitoring of the extent of reaction, revealed that ca. 80% of the arsine had reacted to produce Ph_2MeAsS. Heating was therefore continued for another 6 h, but little change in the product mixture was observed. A dark-brown oil remained when the volatiles were removed. Many attempts to try to crystallize the arsine sulphide from this oil failed. Finally, some HMPA was added, and after seeding with crystal fragments of the $Ph_2MeAsS.HMPA$ adduct, the arsine sulphide crystallised as the adduct in 71% yield, m.p. 90-94 °C (the adduct dissociated into its liquid components on melting and did not re-form on cooling). (Found: C, 50.03; H, 6.70; N, 9.06%. Calc. for $C_{13}H_{13}AsS.\ C_6H_{18}N_3OP$: C, 50.09; H, 6.86; N, 9.23%; M, 455).

Ph_3As + sulphur in o-dichlorobenzene.

Ph_3As (1 g, 3.27 mmol) and an excess of sulphur (0.2 g, 6.25 mmol) were heated in o-dichlorobenzene (10 ml) at temperatures up to 150 °C for 8 h. The volume of the resulting, slightly green-tinted, solution was reduced slowly on the rotary evaporator until a white solid began to appear. This white solid was then filtered, washed with n-pentane, and dried in air to produce 0.65 g of a white, crystalline solid (59.1%), m.p. 165-8 °C (lit. 163.5[56]). (Found: C, 64.1; H, 4.35%. Calc. for $C_{18}H_{15}AsS$: C, 63.91; H, 4.44%; M, 338.)

$Ph_2AsCH_2AsPh_2$ + sulphur in toluene.

$Ph_2AsCH_2AsPh_2$ (3 g, 6.36 mmol) and an excess of sulphur (0.45 g, 14.0 mmol) were refluxed in toluene (40 ml) for 24 h. The mixture was filtered hot and left to recrystallise. No solid separated out, and only when almost all of the toluene was removed, did a slightly yellow solid appear. This, however, proved to be unreacted $Ph_2AsCH_2AsPh_2$ (contaminated with sulphur) as determined by comparison of its ^1H n.m.r. spectrum with that of an authentic sample.

$Ph_2AsCH_2AsPh_2$ + sulphur in o-dichlorobenzene.

The above reaction was repeated in o-dichlorobenzene. Heating in an oil-bath at 150 °C for 14 h resulted in the production of ca. 2.4 g of a crude, white solid. This was recrystallised from benzene (15 ml) to produce a total yield of the diarsine monosulphide, $Ph_2As(S)CH_2AsPh_2$, of 2.2 g (70%), m.p. 136-140 °C (lit. 138-9 °C[65]). I.r. spectrum (KBr), ν(As=S) = 489, 478 cm^{-1}. (Found: C, 59.69; H, 4.36; S, 6.67%. Calc. for $C_{25}H_{22}As_2S$: C, 59.51; H, 4.40; S, 6.36%; M, 504.)

$Ph_2AsC_2H_4AsPh_2$ + sulphur.

$Ph_2AsC_2H_4AsPh_2$ (4 g, 8.23 mmol) and an excess of sulphur (0.55 g, 17.2 mmol) were placed in a three-necked r.b. flask which had been purged with dry N_2 for 1 h. The mixture was heated to ca. 100 °C, at which temperature the diarsine was observed to melt. The resulting suspension of sulphur in the diarsine was heated at 150 °C for 30 min, when the mixture suddenly solidified. Toluene (50 ml) was added to the dark-brown solid mixture, which was filtered when no more solid would dissolve in the boiling toluene. The resulting recrystallised solid was an off-white colour, although the ^1H n.m.r. showed the presence of only one signal in the methylene region (Table 9). Further recrystallisations (from ethanol) did produce pure $Ph_2As(S)C_2H_4As(S)Ph_2$, but the yield had been reduced to only 1.8 g (40%), m.p. 200-3 °C (lit. 200 °C[63]). I.r. (KBr), ν (As=S) = 499 cm^{-1}. (Found: C, 56.9; H, 4.45%. Calc. for $C_{26}H_{24}As_2S_2$: C, 56.73; H, 4.36%; M, 550.)

(ii) Reaction between tertiary arsines and sulphur monochloride, S_2Cl_2.

$Ph_2MeAs + S_2Cl_2$.

S_2Cl_2 (0.5 ml, 6.25 mmol) was vacuum distilled into a solution of Ph_2MeAs (1 ml, 5.2 mmol) in anhydrous ether (10 ml) at -196 °C. When the solution was allowed to warm up, immediate reaction took place, producing a dense, yellow solid. The mixture was stirred for up to 1 h, at room temperature, after which the slight excess of S_2Cl_2 and the ether were distilled off. The resulting bright yellow solid was dissolved as much as possible in chloroform (leaving a yellow solid with a "plastic" consistency). On removing the chloroform, 1.59 g of a yellow-white solid was produced, which was found to be $Ph_2MeAsCl_2$ rather than Ph_2MeAsS (yield, 96%).

No microanalysis of the product was attempted because of the known hygroscopic nature of tertiary arsine dichlorides.[87] The n.m.r. parameters of the compound are contained in Table 9, which indicate the deshielding effect of the two chlorine atoms. The i.r. spectrum of $Ph_2MeAsCl_2$ was run as a nujol mull between KCl plates (4 000-600 cm^{-1}) and polythene discs (600-180 cm^{-1}) since, firstly, strong bands appeared between 2 200 and 3 000 cm^{-1} (due probably to partial hydrolysis of $Ph_2MeAsCl_2$ giving $Ph_2MeAs(OH)Cl$[88]) when the sample was run as an alkali halide disc, and, secondly, halide exchange occurred when CsI or KBr discs were used. A medium strength band at 349 cm^{-1} and a slightly weaker doublet band centred at 310 cm^{-1} may be assigned to a phenyl group vibration and perhaps the As-Cl stretching frequency, respectively.[89]

$Ph_3As + S_2Cl_2$

S_2Cl_2 (0.5 ml, 6.25 mmol) was vacuum distilled into a solution of Ph_3As (1.59 g, 5.2 mmol) in anhydrous ether (20 ml) at -196 °C. When the solution warmed to temperatures sufficient to allow mixing of the two reactants in ether, immediate reaction again occurred, producing an almost quantitative yield of Ph_3AsCl_2 (1.82 g, 93%), after removal of the sulphur by chloroform extraction.

No n.m.r. details are listed in Table 9 for Ph_3AsCl_2 because, possibly as a result of its hygroscopic nature, only very broad, unresolved aromatic resonances were observed between 7.4 and 7.8δ, and between 7.8 and 8.3δ. The i.r. spectrum (run as described above for $Ph_2MeAsCl_2$) exhibited medium-strength bands at 472 and 365 cm^{-1} (Phenyl group vibrations[89]) and a weaker doublet band centred at 310 cm^{-1} (As-Cl stretch ?[89]).

Dropwise addition of S_2Cl_2 to Ph_3As.

Ph_3As (0.5 g, 1.63 mmol) was dissolved in 20 ml of anhydrous ether in a three-necked r.b. flask which was fitted with a pressure-equilibrated dropping funnel and a N_2 inlet/outlet system (the vessel had been purged with dry N_2 prior to the addition of the ether). S_2Cl_2 (130 µl, 1.63 mmol) was added (using a 500 µl syringe) to 20 ml of anhydrous ether in the dropping funnel. The S_2Cl_2 solution was added dropwise to the reaction mixture over a 45 min period. The solution soon changed from clear and colourless to white and cloudy, eventually depositing what appeared to be a white solid, the supernatant liquid becoming yellow coloured. Stirring at room temperature was continued for a further 15 min after the addition was complete. The precipitate was filtered and dried to produce 0.31 g of a yellow-white solid which on extraction with chloroform was found to have been contaminated with elemental sulphur. Further chloroform extractions resulted in the isolation of a white solid (0.25 g, 41%), the ^1H n.m.r. of which indicated that it was not Ph_3AsS, but also that the aromatic resonances were sharper and less well separated than in the product from the vacuum transfer method. Nevertheless, the reaction did not appear to proceed by sulphur transfer, but rather by chlorine transfer from S_2Cl_2 to the arsine.

Dropwise addition of S_2Cl_2 to $Ph_2As(S)CH_2AsPh_2$.

An ether solution of S_2Cl_2 (160 µl, 2.0 mmol) was added dropwise to a stirred ether solution of $Ph_2As(S)CH_2AsPh_2$ (1 g, 2.0 mmol) in a three-necked r.b. flask. Stirring at room temperature was continued for a further 2 h before the yellow-white solid which had deposited was filtered off. After extraction with chloroform to remove the elemental sulphur, 0.7 g (61%) of what was thought to be $Ph_2As(S)CH_2AsPh_2Cl_2$ was isolated. The ^1H n.m.r. consisted of a singlet at δ4.35 (slightly broadened) and

two very broad unresolved aromatic resonances between 7.3 and 7.8 δ, and between 7.8 and 8.2 δ.

(iii) Reaction between $Ph_2MeAsCl_2$ and H_2S.

$Ph_2MeAsCl_2$ (1 g, 3.18 mmoles) was dissolved (not completely) in ethanol (25 ml) and hydrogen sulphide (generated by the slow addition of dilute sulphuric acid to a solution of sodium sulphide in water) was bubbled through the solution for 1 h. Any insoluble material was filtered off and after removal of the solvent, the filtrate yielded a viscous, green-tinted liquid, the ^1H n.m.r. of which revealed that it was almost exclusively Ph_2MeAsS.

After attempts to recrystallise the arsine sulphide from a variety of solvents had failed, a vacuum distillation of the oil was tried in order to isolate a pure sample for microanalysis. Using the apparatus described on p.71, the oil was vacuum distilled (120 °C, 0.06 mm) for a few hours, but the yellow liquid which initially collected rapidly turned deep-brown in colour. A ^1H n.m.r. of the distillate showed that the arsine sulphide had decomposed to the arsine to an appreciable extent.

(iv) Sulphur exchange reaction between Ph_3AsS and Ph_2MeAs.

Ph_3AsS (26 mg, 0.08 mmol) and Ph_2MeAs (15 µl, 0.08 mmol) were mixed together in deuteriochloroform in a n.m.r. tube. On allowing the mixture to stand at room temperature for 19 h, an equilibrium mixture of Ph_3As, Ph_2MeAsS, Ph_2MeAs, and Ph_3AsS was found to have been produced, as determined by the observation of signals due to all four of these components in the ^1H n.m.r. spectrum (see Table 9). Addition of more Ph_3AsS (a total of 13 mg) had little further effect on the equilibrium position, but at least ca. 85% of Ph_2MeAs had been converted to Ph_2MeAsS

by sulphur transfer from Ph_3AsS.

It was discovered that Ph_3As could be sublimed out of a PH_3AsS/Ph_3As solid mixture by heating (under vacuum, 0.06 mm) at temperatures between 60 ^{o} and 80 ^{o}C. The products of the n.m.r. tube sulphur transfer reaction were therefore placed in a cold-finger sublimation unit and evacuated (0.06 mm). They were immersed in an oil-bath preheated to 75 ^{o}C, and heating at temperatures up to a maximum of 82 ^{o}C was continued for 1 h. A viscous, colourless liquid, however, condensed on the cold finger rather than the expected white solid (Ph_3As), and a ^{1}H n.m.r. of the solid residue revealed that the equilibrium had reversed, reforming Ph_3AsS with only slight traces of Ph_3As and Ph_2MeAsS remaining. The condensed liquid was obviously the most volatile component, Ph_2MeAs.

(v) Ph_2RAs + selenium.

Equimolar amounts of the arsines, Ph_2RAs (R=Me,$C_2H_4AsPh_2$) and elemental selenium, were placed in separate n.m.r. tubes to which deuteriobenzene had been added. The mixtures were both heated at 80 ^{o}C for 20 h, but only a broadening of the methyl or methylene resonances was observed. The mixtures were decanted into fresh n.m.r. tubes to remove the powdered selenium, and again only broadened signals were detected. No further attempts were made to produce any tertiary arsine selenides.

(B) Adducts of tertiary phosphine and arsine chalcogenides.

Ph_3PS + $(MeO)_3$ PO

Ph_3PS (0.5 g, 1.7 mmol) was dissolved in a solvent mixture consisting of $(MeO)_3$ PO (1 ml) and benzene (2 ml). The benzene was allowed to slowly evaporate, and it was observed that clear, colourless needles soon formed. These were filtered, washed with n-pentane (to remove any surface moisture), and dried in air to constant weight (0.15 g). A ^{1}H n.m.r. of this solid showed only the presence of Ph_3PS, no signals due

to the methyl protons of $(MeO)_3$ PO being observed. No further attempts were made to produce a $Ph_3PS.(MeO)_3$ PO adduct.

Ph_3AsS + $(Me_2N)_3$ PO (HMPA).

Ph_3AsS (0.2 g, 0.59 mmol) was dissolved in a solvent mixture consisting of HMPA (0.5 ml) and benzene (1 ml) by heating at 85 °C for a few minutes (preheated oil bath). No solid recrystallised overnight but on scratching the solution, precipitation resulted. The white solid was filtered, washed with n-pentane, and dried in air to constant weight (0.09 g). No adduct was found to have been formed, the ^1H n.m.r. of the solid indicating the presence of Ph_3AsS alone. No further attempts were made to isolate a Ph_3AsS.HMPA adduct.

CHAPTER 3

CHALCOGEN EXCHANGE REACTIONS OF ORGANOPHOSPHORUS COMPOUNDS

INTRODUCTION

Chalcogen Exchange Reactions of Organophosphorus Compounds.

(a) Sulphur Exchange.

The transfer of sulphur atoms from tertiary phosphine sulphides to more basic phosphine molecules is well documented, and finds numerous synthetic applications (equation 73)[90].

$$R_3PS + R^1_3P \xrightarrow{\Delta} R_3P + R^1_3PS \qquad (73)$$

In the preparation of tertiary phosphine sulphides, the sulphur, as well as reacting directly with tertiary phosphines, can also be donated by sulphur transfer agents. Thus tertiary phosphine sulphides can act as sources of sulphur, and in many cases it is the desulphurised phosphine which is the required product.

It has been found, for example, that tetramethylbiphosphine disulphide can be desulphurised with tributylphosphine to give the biphosphine in 69% yield (equation 74)[91].

$$Me_2P(S)P(S)Me_2 + 2\ Bu_3P \xrightarrow{130\ ^oC} Me_2PPMe_2 + 2\ Bu_3PS \qquad (74)$$

A kinetic study[92] of reaction 73, (R=Ph,R^1=^{n}Bu), suggested that the sulphur transfer was a concerted process involving a transition state in which the sulphur was bonded to both phosphorus atoms.

Thiophosphoryl chloride, $PSCl_3$, was first used as a sulphur transfer agent in 1932[93]. Lindner and Beer[64] discovered that $PSCl_3$ could transfer sulphur to tertiary and ditertiary phosphines and arsines simply by dissolving the phosphine or arsine in an excess of $PSCl_3$ (the latter functioning as a solvent as well as a reactant) and stirring at room temperature for a few hours [equation (75); R=Et,Ph,$(CH_2)_n MPh_2$(n=0,1,2); R^1=Et,Ph; M=P,As].

$$RR^1_2M + PSCl_3 \longrightarrow RR^1_2MS + PCl_3 \qquad (75)$$

The reaction was almost quantitative, producing a product of high purity because side reactions, which reduce the yields of the reaction of elemental sulphur with phosphines and arsines, were essentially eliminated by using $PSCl_3$ as the solvent in moisture-free conditions. Triphenylarsine, in contrast to the other phosphines and arsine, required to be heated for 20 h at 140 °C to go to completion[64].

Ellerman and Schirmacher[94] used $PSCl_3$ to prepare the tetra-tertiary phosphine sulphide, $C(CH_2P(S)Ph_2)_4$, which could otherwise not be obtained in a pure state.

An extension of these sulphur-exchange reactions was reported in 1975 by Grim and Mitchell[95], who studied the redistribution of sulphur in unsymmetrical methylene diphosphine monosulphides (equation 76).

$$Ph_2P(S)CH_2PMe_2 \xrightarrow[\text{diglyme}]{160\ ^\circ} Ph_2PCH_2P(S)Me_2 \qquad (76)$$

Thus heating at 160 °C for 30 h caused the sulphur atom to move from the less basic phosphorus atom to the more basic. Preliminary kinetic experiments indicated that the reaction was neither simple first order (as would be expected from an intramolecular sulphur transfer), nor simple second order. They also identified two compounds, $Ph_2P(S)CH_2(S)PMe_2$ and $Ph_2PCH_2PMe_2$, as being present in approximately equal and constant amounts ($<$ 10% each of total products) throughout the course of the reaction, after a brief initiation period. The mechanism of the sulphur transfer was thought to be rather complex.

(b) Selenium and Tellurium Exchange.

Surprisingly, there have been no reports of selenium transfer between phosphorus atoms in the literature.

According to Zingaro and co-workers,[50] tellurium dissolved in

toluene solutions of trialkyl phosphines, aryldialkyl phosphines and, to a limited extent, in alkyldiaryl phosphines. It was completely insoluble in a triphenyl phosphine solution. The solubility of Te in the various phosphines thus parallels their chemical reactivity, i.e. the solubility decreases as the nucleophilic character of the phosphine decreases. No diphenylalkyl phosphine tellurides could be isolated although the slight solubility of tellurium in this type of phosphine indicated that the reactions may have proceeded to some extent producing an equilibrium mixture, the phosphine telluride being too unstable to be isolated. The extent to which the reaction proceeded clearly diminished as the number of phenyl groups on the phosphorus atom increased.

Austad et al.,[96] isolated $(Ph_3P)_2Te$ in 30% yield when tetraphenylarsonium tellurocyanate in acetonitrile was treated with triphenylphosphine in the presence of lithium perchlorate (equation 77).

$$TeCN^- + 2Ph_3P \rightleftharpoons (Ph_3P)_2Te + CN^- \qquad (77)$$

The compound was stable in the solid state in sunlight and moist air, but decomposed on heating at 83-85 °C and upon dissolution in various solvents unless excess triphenylphosphine was present. An X-ray structure determination of the adduct revealed a linear P-Te-P configuration with a "normal" bond between tellurium and one of the phosphorus atoms (2.4 Å), whereas the interaction between tellurium and the other phosphorus atom was quite weak (3.5 Å). They suggested that the reason for the non-existence of Ph_3PTe and the stability of the $(Ph_3P)_2Te$ adduct might be that Ph_3PTe was polarized like $Ph_3\overset{-}{P}\text{-}\overset{+}{Te}$ in view of the low electronegativity of tellurium relative to phosphorus in triphenylphosphine. This implied that Ph_3PTe was the acceptor in the interaction with Ph_3P.

RESULTS AND DISCUSSION

(A) Rapid transfer of tellurium from tertiary phosphine tellurides to tertiary phosphines.

The photolysis of dibenzyl ditelluride in the presence of diphenylmethylphosphine in deuteriobenzene produced dibenzyl monotelluride and elemental tellurium at a slightly faster rate than in the absence of the phosphine. Tellurium deposition on the walls of the n.m.r. tube continued for some time after irradiation was interrupted. These differences were accounted for by the formation of some diphenylmethylphosphine telluride, the decomposition of which to phosphine and tellurium is accelerated by glass surfaces (Chapter 1, p. 48).

No separate ^1H n.m.r. signals for the phosphine telluride were observed at ambient temperatures, but a single methyl doublet was found, shifted downfield from the position of Ph_2MeP itself, and with a reduced coupling constant (sometimes to zero). This indicated the rapid transfer of tellurium between Ph_2MePTe and Ph_2MeP (equations 78 and/or 79; R_3=Ph_2Me).

$$R_3PTe \underset{\text{fast}}{\rightleftharpoons} R_3P + Te \qquad (78)$$

$$R_3PTe + R_3P \underset{\text{fast}}{\rightleftharpoons} R_3P + R_3PTe \qquad (79)$$

Variable temperature n.m.r. measurements on this system showed that the equilibrium was temperature dependent. As the temperature was increased from 35 ^{o} to 85 ^oC, the coupling constant, $^2J_{PH}$, increased from ca. 1 Hz to a maximum of 2.3 Hz (the coupling constant for pure Ph_2-MeP is 3.9 Hz in C_6D_6) and the methyl doublet moved about 8 Hz upfield (relative to the methyl doublet of Ph_2MePO, present in the mixture as a standard). On allowing the deuteriobenzene solution to cool to 35 ^oC, the coupling constant decreased and the methyl doublet shifted downfield

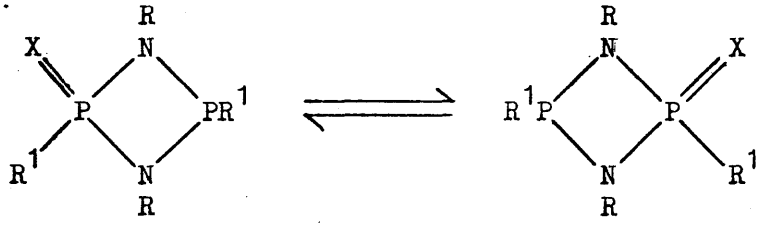
again, but neither reattained their original values.

The irreproduceability of the v.t. effects suggests that R_3PTe may be decomposing according to (78), but not completely reversibly. In partial support of this, attempts to produce similar solutions by heating a mixture of the phosphine and powdered tellurium in deuteriobenzene failed, due probably to the heterogeneous nature of the system.

This evidence suggests that (78) operates in this system, and might be responsible for the v.t. n.m.r. observations with or without an intermolecular tellurium transfer not involving free Te (equilibrium 79). Only (78) involves free atomic tellurium. These atoms may either recombine with Ph_2MeP to form Ph_2MePTe, or precipitate as elemental tellurium (which would account for the irreproduceability). Therefore, increasing the temperature will push (78) over to the right, the increased amount of Ph_2MeP present (relative to Ph_2MePTe) accounting for the upfield chemical shift movement. Reducing the temperature will reverse this process, increasing the relative amount of Ph_2MePTe present (unless the tellurium atoms deposit as the bulk element). The reduction in coupling constant as the temperature is decreased is probably because $^2J_{PH}$ for Ph_2MePTe is negative (the analogous phosphine selenide has a negative coupling constant[97]) whereas $^2J_{PH}$ for Ph_2MeP is likely to be positive.[98] At ambient temperatures (35 °C) the transfer is fast on the n.m.r. time scale, so that reducing the temperature to below ambient should slow it down eventually to a point where separate signals due to Ph_2MePTe are observable. (No attempt was made to reduce the temperature to below ambient since C_6D_6 freezes at 5 °C and, as described earlier, attempts to produce similar solutions from the phosphine and elemental tellurium failed.) It should be emphasised, however, that although the operation of (78) in this Ph_2MePTe/Ph_2MeP system is indicated, the

concurrent operation of (79) at all times cannot be discounted. Indeed, after the completion of this work, a note by Du Mont and Kroth[52] described a similar system not involving free tellurium, in which nucleophilic attack of R_3P at tellurium in R_3PTe was postulated, producing a linear intermediate of the type $R_3P\text{-}Te\text{-}PR_3$. (Austad isolated a compound of this type with R=Ph.[96]) They proposed (79) to account for the tellurium transfer in their particular R_3PTe/R_3P ($R={}^tBu, Me_2N$) system, but apparently did not consider the possibility of atomic tellurium being involved. The more stable phosphine tellurides involved in their work may explain why elemental tellurium was produced in our system only, since phosphine tellurides are known to be unstable when phenyl groups are attached to phosphorus.[50,51]

Subsequently, Scherer and Schnabl[99] reported the fast exchange of tellurium in a cyclodiphosphazane system (equation 80; R=Me, $R^1={}^tBu$; X=Te).



(80)

The tellurium transfer was fast on the n.m.r. time scale at ambient temperatures but was noticeably slowed down by lowering the temperature. The coalescence temperature was found to be concentration dependent indicating that both intra- and inter-molecular exchange might be occurring. However, no cyclodiphosph(III)azane itself was detected, low temperature ^1H and ^{31}P n.m.r. spectra both showing the presence of the above <u>cis</u>-monotelluride alone. (Formation of a mixture of the cyclodiphosph(III)-azane and its monotelluride is conceivable for intermolecular tellurium exchange.)

Keat and Thompson[100] also reported an exchange of tellurium in another cyclodiphosphazane system (equation 80; R=^{t}Bu, R^{1}=NMe_2; X=Te). The exchange was at an intermediate rate on the n.m.r. time-scale at ambient temperatures but was appreciably slowed down when the solution ($CDCl_3$) was cooled to -60 °C. The exchange process was found to be concentration dependent, suggesting that the tellurium transfer was at least partly intermolecular.

(B) Rapid transfer of selenium from tertiary phosphine selenides to tertiary phosphines.

We have found that the exchange of selenium between tertiary phosphine selenides and the analogous tertiary phosphine is fast on the n.m.r. time-scale at elevated temperatures (Table 10). Thus the two methyl signals, produced after ^{31}P decoupling, of mixtures of Ph_2MePSe and Ph_2MeP broaden and coalesce as the temperature is increased. (We define the coalescence temperature as the lowest temperature at which no valley can be discerned between the individual signals.) The coalescence covers a wide range of temperatures and is difficult to measure accurately, but it is obviously concentration dependent. The methylene signals from the mixtures of $Ph_2P(Se)CH_2PPh_2$ and $Ph_2PCH_2PPh_2$, and of $Ph_2P(Se)C_2H_4P(Se)Ph_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ display similar behaviour. This is consistent with an intermolecular transfer of selenium. Although the coalescence temperatures of Ph_2MePSe with Ph_2MeP and $Ph_2P(Se)CH_2PPh_2$ with $Ph_2PCH_2PPh_2$ are comparable, 1,2-bis-(diphenylphosphino)ethane with its mono- and di-selenide coalesced at lower temperatures, and $Ph_2P(Se)CH_2PPh_2$ alone or with $Ph_2P(Se)CH_2P(Se)Ph_2$ failed to reach coalescence in the temperature range examined. Obviously the nature of the substituents on phosphorus affects the rate of selenium exchange.

N.m.r. investigations also show that equimolar solutions of Ph_2P-

Table 10 Coalescence Temperatures[a]

Components	Concentrations[b]/mol l^{-1} (Coalescence temp./K)							
Ph_2MePSe	0.33	(>447)	0.36	(438)	0.67	(428)	1.0	(418)
Ph_2MeP	0.33		0.72		1.32		2.0	
$Ph_2P(Se)CH_2PPh_2$	0.53	(>438)						
$Ph_2P(Se)CH_2PPh_2$	0.53	(438)	0.67	(418)	1.0	(411)		
$Ph_2PCH_2PPh_2$	0.27		0.67		1.0			
$Ph_2P(Se)CH_2P(Se)Ph_2$	0.67	(>443)						
$Ph_2P(Se)CH_2PPh_2$	0.67							
$Ph_2P(Se)C_2H_4P(Se)Ph_2$	0.20		0.33					
$Ph_2P(Se)C_2H_4PPh_2$	0.40	(398[c])	0.67	(368)				
$Ph_2PC_2H_4PPh_2$	0.20		0.33					

[a] Measured at 60 MHz on a JEOL C60HL spectrometer with noise-modulation of the ^{31}P irradiation field (P^V and P^{III} signals generally separated by ca. 1 KHz). Temperatures ± 10 K. [b] o-Dichlorobenzene solutions. [c] Chlorobenzene solution.

$(Se)CH_2P(Se)Ph_2$ and $Ph_2PCH_2PPh_2$ react quantitatively to produce $Ph_2P(Se)CH_2PPh_2$ immediately on mixing, whereas $Ph_2P(Se)C_2H_4P(Se)Ph_2$ and $Ph_2PC_2H_4PPh_2$ equilibrate to a 1:2:1 mixture of $Ph_2P(Se)C_2H_4P(Se)Ph_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ at a similar rate. This difference in the nature of the products is presumably because the more electron deficient P(V) atom affects the activity of the P(III) atom in $Ph_2P(Se)CH_2PPh_2$ more than in $Ph_2P(Se)C_2H_4PPh_2$, since in the latter the phosphorus atoms are separated by two CH_2 groups. (Mann[101] proposed a similar inductive deactivation effect to explain the weakness of the attachment of one sulphur atom in $PhBuAs(S)C_2H_4As(S)PhBu$ resulting in a change of configuration at one arsenic atom on mild heating.)

Keat and Thompson[100] recently noted that, as with $Ph_2P(Se)CH_2PPh_2$ in this work, the cyclodiphosphazane monoselenide (equation 80; R=Me, R^1= ^tBu; X=Se) could be quantitatively produced within several minutes of mixing equivalent amounts of its analogous diselenide and cyclodiphosph (III) azane in benzene. However, the monoselenide did not exhibit selenium exchange on the n.m.r. time-scale even when heated to 140 °C.

We have found that the analogous reactions of phosphine sulphides are similar, although much slower (equations 81 and 82).

$$Ph_2P(S)CH_2P(S)Ph_2 + Ph_2PCH_2PPh_2 \rightleftharpoons 2\ Ph_2P(S)CH_2PPh_2 \quad (81)$$

$$Ph_2P(S)C_2H_4P(S)Ph_2 + Ph_2PC_2H_4PPh_2 \rightleftharpoons Ph_2P(S)C_2H_4PPh_2 \quad (82)$$

Equilibrium is reached after about 24 h at 160 °C (in the absence of solvent, or in o-dichlorobenzene solution) but requires more than 40 days at 80 °C in benzene solution. When $Ph_2P(S)CH_2PPh_2$ (ca. 100 mg) was heated (under vacuum) at 146-156 °C for 6 h in a sublimation apparatus, the sublimed material (ca. 20 mg) was found to consist of $Ph_2PCH_2PPh_2$ and a

small amount of $Ph_2P(S)CH_2PPh_2$. The residue (ca. 80 mg) consisted of $Ph_2P(S)CH_2PPh_2$ (80%), $Ph_2P(S)CH_2P(S)Ph_2$ (16%), and $Ph_2PCH_2PPh_2$ (4%), indicating that equation (81) is reversible, although removal of any Ph_2P-CH_2PPh_2 produced by sublimation is presumably necessary to pull equation (81) over to the left, since heating a benzene solution of $Ph_2P(S)CH_2PPh_2$ for 7 days at 80 °C failed to produce any $Ph_2P(S)CH_2P(S)Ph_2$ or $Ph_2PCH_2PPh_2$.

Further selenium exchange studies.

An attempt was made to synthesize the previously unreported mixed dichalcogenide [(diphenylphosphinoselenoyl)-methyl] diphenylphosphine sulphide, $Ph_2P(Se)CH_2P(S)Ph_2$, by reacting $Ph_2PCH_2P(S)Ph_2$ with powdered black selenium. The mixture (1:1) was refluxed in benzene for 19 h, and resulted in the isolation of a solid, crystalline mixture consisting of $Ph_2P(Se)$-$CH_2P(S)Ph_2$ plus $Ph_2P(S)CH_2P(S)Ph_2$ (ca. 3:1, respectively), with a trace of unreacted $Ph_2PCH_2P(S)Ph_2$. A triplet centred at δ4.13 in the ^1H n.m.r. of this solid mixture was assigned to $Ph_2P(Se)CH_2P(S)Ph_2$ because the chemical shift was intermediate between that found for $Ph_2P(Se)CH_2P(Se)Ph_2$ and $Ph_2P(S)CH_2P(S)Ph_2$ (Table 11, p.106).

The formation of $Ph_2P(S)CH_2P(S)Ph_2$ could not be readily explained, so it was decided to repeat the reaction in a n.m.r. tube (on a smaller scale) and to closely monitor its progress. A 1:1 mixture of $Ph_2PCH_2P(S)$-Ph_2 and selenium in $CDCl_3$/T.M.S. was therefore added to a n.m.r. tube and after standing for 3 h at room temperature, a 1:1 mixture of $Ph_2P(Se)CH_2$-$P(S)Ph_2$ and unreacted $Ph_2PCH_2P(S)Ph_2$ had been produced. The solution, however, required a further four days at room temperature before all the $Ph_2PCH_2P(S)Ph_2$ reacted to give $Ph_2P(Se)CH_2P(S)Ph_2$ exclusively (equation 83). No triplet due to the methylene protons of $Ph_2P(S)CH_2P(S)Ph_2$ (Table 11) was detected at any time during this reaction.

$$Ph_2PCH_2P(S)Ph_2 + Se \xrightarrow{R.T.} Ph_2P(Se)CH_2P(S)Ph_2 \qquad (83)$$

The n.m.r. tube reaction between $Ph_2P(Se)CH_2PPh_2$ and elemental sulphur was similarly studied. After standing for 4 h at room temperature, the methylene resonance of $Ph_2P(Se)CH_2PPh_2$ had diminished in size, and signals due to the methylene protons of $Ph_2P(Se)CH_2P(Se)Ph_2$, $Ph_2P(Se)CH_2P(S)Ph_2$, $Ph_2P(S)CH_2P(S)Ph_2$, and $Ph_2PCH_2P(S)Ph_2$ were all observed. The two monosubstituted diphosphines soon disappeared as they reacted completely with the sulphur. The final products consisted of a 1:2:1 mixture of $Ph_2P(Se)CH_2P(Se)Ph_2$, $Ph_2P(Se)CH_2P(S)Ph_2$, and $Ph_2P(S)CH_2P(S)Ph_2$, respectively (equation 84).

$$4\ Ph_2P(Se)CH_2PPh_2 + 4\ S \xrightarrow{R.T.} Ph_2P(Se)CH_2P(Se)Ph_2 + 2\ Ph_2P(Se)CH_2P(S)Ph_2 + Ph_2P(S)CH_2P(S)Ph_2 \qquad (84)$$

The product mixture in equation (84) was thought to arise from intermolecular selenium exchange between the initially formed $Ph_2P(Se)CH_2P(S)Ph_2$ and $Ph_2P(Se)CH_2PPh_2$ (equation 85).

$$Ph_2P(Se)CH_2P(S)Ph_2 + Ph_2P(Se)CH_2PPh_2 \rightleftharpoons Ph_2PCH_2P(S)Ph_2 + Ph_2P(Se)CH_2P(Se)Ph_2 \qquad (85)$$

A 1:1 mixture of the compounds on the right-hand-side (R.H.S.) of equation (85) was, therefore, dissolved in $CDCl_3$ and within twenty minutes the equilibrium state of an approximately 2:1 mixture of the L.H.S. to R.H.S. components of equation (85) was attained.

Therefore, a product mixture results from the reaction of $Ph_2P(Se)CH_2PPh_2$ with sulphur, because selenium exchange between $Ph_2P(Se)CH_2P(S)Ph_2$ and $Ph_2P(Se)CH_2PPh_2$ gives rise to two new compounds (equation 85). In contrast, $Ph_2P(Se)CH_2P(S)Ph_2$ is produced exclusively in the reaction of $Ph_2PCH_2P(S)Ph_2$ with selenium, because selenium exchange between Ph_2-

$P(Se)CH_2P(S)Ph_2$ and $Ph_2PCH_2P(S)Ph_2$ will give rise to no new compounds, and sulphur exchange obviously does not occur rapidly at room temperature (although as the benzene reflux reaction shows, it may occur to some extent at elevated temperatures).

When a slight excess of $Ph_2PCH_2PPh_2$ was added to an o-dichlorobenzene solution of $Ph_2P(Se)CH_2P(S)Ph_2$ in a n.m.r. tube, the monosubstituted diphosphines, $Ph_2P(Se)CH_2PPh_2$ and $Ph_2PCH_2P(S)Ph_2$, were produced quantitatively in equal amounts (equation 86).

$$Ph_2P(Se)CH_2P(S)Ph_2 + Ph_2PCH_2PPh_2 \xrightarrow{R.T.} Ph_2P(Se)CH_2PPh_2 + Ph_2PCH_2P(S)Ph_2 \quad (86)$$

No signals due to $Ph_2P(Se)CH_2P(Se)Ph_2$, arising from selenium exchange between $Ph_2P(Se)CH_2P(S)Ph_2$ and $Ph_2P(Se)CH_2PPh_2$ (equation 85), were detected because of its known immediate reaction with the diphosphine (which was in excess) to produce $Ph_2P(Se)CH_2PPh_2$.

The redistribution of sulphur, selenium, and tellurium[102] between phosphorus atoms in methylene diphosphine systems thus appears to be a general process of which reaction (76), (p. 93), is but a specific example. Seen in this light, the detection of approximately 10% of $Ph_2P(S)CH_2P(S)Me_2$ and $Ph_2PCH_2PMe_2$ amongst the products of reaction (76) is not remarkable[95], and the same workers subsequently reported that a mixture of $Ph_2P(S)CH_2P(S)Me_2$ and $Ph_2PCH_2PMe_2$ did indeed produce $Ph_2P(S)CH_2PMe_2$ in good yield.[103]

The rate of chalcogen atom transfer between phosphines is seen from the above results to increase in the order S $\ll$ Se $<$ Te.

Some interesting synthetic applications of the fast exchange of selenium between phosphorus atoms can be envisaged. The protection of a P(III) atom during one or many of the various reaction stages of the

synthesis of a complex phosphorus containing molecule may be better performed by making the P(V) selenide derivative rather than the sulphide derivative. The ready formation of the often quite stable P(V) selenide, coupled with the easy removal of the selenium atom by an exchange reaction at room temperature with a more basic P(III) molecule seems a much more attractive alternative to the more commonly used sulphur protection method, which, although the sulphide derivative may be slightly more stable than the corresponding selenide derivative, usually involves heating at elevated temperatures to effect the exchange of sulphur to a more basic P(III) molecule. The formation of the diphosphine diselenide, $Me_2P(Se)P(Se)Me_2$, for example, may be a better means of protecting the spontaneously inflammable Me_2PPMe_2 than making the analogous disulphide, since the latter required heating at 130 ^{o}C with 2 equivalents of $^{n}Bu_3P$ to reform the diphosphine in 69% yield (equation 74), whereas the analogous deselenation reaction may only require stirring the two reactants at ambient temperatures.

The synthesis of mixed dichalcogenides with the general formula $R^1R^2P(X)CH_2P(Y)R^3R^4$ (R^1-R^4, alkyl or aryl groups; X=Se, Y=S) from the corresponding methylene diphosphines will require the addition of the sulphur atom first, then the selenium atom, since the reverse addition procedure would result in the formation of a mixture of all three possible dichalcogenides by the occurrence of rapid intermolecular selenium exchange between $R^1R^2P(Se)CH_2P(S)R^3R^4$ and unreacted $R^1R^2P(Se)CH_2PR^3R^4$.

Experimental.

The spectroscopic instrumentation used was as described in the experimental section of Chapter 1 (p.52).

The tertiary phosphines used in this work were obtained commercially from Strem Chemicals Inc., Fluorochem Ltd., or the Maybridge Chemical Company. $Ph_2P(Se)CH_2P(Se)Ph_2$ and $Ph_2P(Se)C_2H_4P(Se)Ph_2$ were prepared

by the reaction of their respective diphosphines with an excess of powdered black selenium in refluxing benzene solution. The analogous phosphine sulphides, $Ph_2P(S)CH_2P(S)Ph_2$ and $Ph_2P(S)C_2H_4P(S)Ph_2$, were prepared similarly by refluxing the diphosphines with an excess of sulphur. $Ph_2P(Se)CH_2PPh_2$ was prepared when required by the dissolution of equivalent amounts of $Ph_2P(Se)CH_2P(Se)Ph_2$ and $Ph_2PCH_2PPh_2$ in an appropriate solvent.

The coalescence temperature studies on mixtures of tertiary phosphine selenides and their analogous tertiary phosphines generally involved the addition of weighed amounts of the various components (when solids) to n.m.r. tubes, followed by evacuation, letting the system down to dry nitrogen, and finally adding the solvent (o-dichlorobenzene or chlorobenzene) against a counter-current of nitrogen. The tubes were capped to maintain the nitrogen atmosphere prior to study but the caps were generally removed during high temperature runs to prevent an explosion from a pressure build-up. Mixtures of Ph_2MePSe and Ph_2MeP (both liquids) were prepared by adding the appropriate amount of the phosphine to a weighed amount of selenium powder in a nitrogen-filled n.m.r. tube. The solvent was then added and the mixture heated briefly with a hair-dryer until all the selenium had reacted.

N.m.r. spectra were run first at ambient temperatures, then at gradually increasing temperatures until the coalescence point was reached. The solution was then allowed to cool to ambient temperatures again to ensure that the exchange was reversible and that the original mixture was essentially unchanged. The relevant n.m.r. characteristics of the compounds studied in this chapter are listed in Table 11.

Preparation of $Ph_2P(S)CH_2PPh_2$

$Ph_2PCH_2PPh_2$ (7.62 g, 0.02 mmol) was dissolved in benzene (150 ml)

Table 11

Selected n.m.r. characteristics of some tertiary phosphine derivatives used in the investigation of sulphur/selenium exchange processes.

Compound	N.m.r. characteristics
Ph_2MePSe	CH_3, 2.25 (d); $^2J_{PH}$ 13.2 Hz ^{31}P, + 23.3
Ph_2MeP	CH_3, 1.47 (d); $^2J_{PH}$ 4.0 Hz ^{31}P, - 26.9
$Ph_2P(Se)CH_2P(Se)Ph_2$	CH_2, 4.30 (t); $^2J_{PH}$ 13.2 Hz ^{31}P, + 22.4
$Ph_2P(Se)CH_2PPh_2$ [b]	CH_2, 3.42 (d/d); $^2J_{P(III)H}$ 0.9 Hz, $^2J_{P(V)H}$ 13.4 Hz; $^{31}P(III)$, - 26.6, $^{31}P(V)$, + 30.5; $^2J_{PP}$ + 83($\pm$ 2) Hz [c]
$Ph_2PCH_2PPh_2$ [b]	CH_2, 2.80 (t); $^2J_{PH}$ 1.9 Hz ^{31}P, - 22.0
$Ph_2P(Se)C_2H_4P(Se)Ph_2$	CH_2, 3.03 (d)[d]; $^2J_{PH}$ + $^3J_{PH}$ 2.0 Hz[e]
$Ph_2P(Se)C_2H_4PPh_2$	CH_2, 2.55 (d)[d]; $^2J_{PH}$ + $^3J_{PH}$ 3.8 Hz[e]
$Ph_2PC_2H_4PPh_2$	CH_2, 2.18 (t)[f]; $^2J_{PH}$ + $^3J_{PH}$ 8.4 Hz[e]
$Ph_2P(S)CH_2P(S)Ph_2$	CH_2, 3.95 (t); $^2J_{PH}$ 13.4 Hz
$Ph_2P(S)CH_2PPh_2$ [b]	CH_2, 3.25 (d/d); $^2J_{P(III)H}$ 0.9 Hz, $^2J_{P(V)H}$ 13.4 Hz; $^{31}P(III)$, - 27.3, $^{31}P(V)$, + 39.2; $^2J_{PP}$ + 73($\pm$ 3) Hz[c]
$Ph_2P(S)C_2H_4P(S)Ph_2$	CH_2, 2.85 (d)[d]; $^2J_{PH}$ + $^3J_{PH}$ 2.0 Hz[e]
$Ph_2P(S)C_2H_4PPh_2$	CH_2, 2.47 (d)[d]; $^2J_{PH}$ + $^3J_{PH}$ 3.0 Hz[e]
$Ph_2P(S)CH_2P(Se)Ph_2$	CH_2, 4.13 (t); $^2J_{PH}$ 13.4 Hz

contd./

Table 11 (contd.)

[a] In o-dichlorobenzene unless otherwise stated. Proton chemical shifts (δ/p.p.m.) relative to internal $SiMe_4$. (d) = doublet, (d/d) = doublet of doublets, and (t) = triplet. Phosphorus chemical shifts are relative to external H_3PO_4, and were calculated from the ^{31}P decoupling frequencies in the ^1H n.m.r. spectra. Positive shifts are downfield from H_3PO_4. [b] In C_6D_6. [c] The sign of $^2J_{PP}$ was found to be opposite to the signs of $^2J_{P(III)H}$ and $^2J_{P(V)H}$, which, for the latter, are known to be negative (ref. 97), the former are usually small and positive, but can be negative (ref. 98). [d] broadened doublet [e] See, e.g., A.J. Carty and R.K. Harris, Chem. Comm., 1967, 234. [f] Deceptively simple methylene proton spectrum, which resembles a 1:2:1 triplet (see ref. in footnote e).

in a three-necked r.b. flask (250 ml) which had been flushed out with dry N_2. Sulphur (0.64 g, 0.02 mmol) was added to the solution in small amounts at room temperature, allowing each portion to react before adding the next. After the addition of one equivalent of sulphur, an aliquot was removed from the reaction mixture to determine the extent of reaction. Integration of the methylene region of the ^1H n.m.r. spectrum revealed that an approximately 1:5:1 mixture of $Ph_2P(S)CH_2P(S)Ph_2$, $Ph_2P(S)CH_2PPh_2$, and $Ph_2PCH_2PPh_2$, respectively, had been produced. More sulphur (0.15 g) was added in 50 mg amounts until all the diphosphine had reacted, leaving a mixture of $Ph_2P(S)CH_2PPh_2$ and $Ph_2P(S)CH_2P(S)Ph_2$ (ca. 3:1). The monosulphide was separated from the disulphide by repeated extractions from hot ether (the disulphide was almost insoluble in hot ether). Recrystallisation from ethanol yielded a total of 3.95 g of $Ph_2P(S)CH_2PPh_2$ (contaminated slightly with $Ph_2P(S)CH_2P(S)Ph_2$), m.p. 85-7 °C (lit. 103-5 °C[104]). (Found: C, 70.71; H, 5.26; P, 16.01; S, 8.29%. Calc. for $C_{25}H_{22}P_2S$: C, 72.11; H, 5.28; P, 14.92; S, 7.69%.

Attempted preparation of $Ph_2P(S)C_2H_4PPh_2$

$Ph_2PC_2H_4PPh_2$ (7.9 g, 0.02 mmol) was dissolved in benzene and one equivalent of sulphur (0.64 g, 0.02 mmol) added in small amounts as described above for $Ph_2PCH_2PPh_2$, except that heating at 50 °C became necessary after a short while to keep the relatively insoluble $Ph_2P(S)C_2H_4P(S)Ph_2$ in solution. More sulphur (0.39 g) required to be added in small amounts to react all the diphosphine, leaving a final mixture of $Ph_2P(S)C_2H_4PPh_2$ plus $Ph_2P(S)C_2H_4P(S)Ph_2$ (ca. 1:3). The reaction mixture was allowed to cool, the disulphide precipitating and being filtered off. The solvent was removed from the filtrate leaving a white solid (ca. 0.6 g) which, when recrystallised from ethanol, was found to consist of an approximately 1:2:1 mixture of $Ph_2P(S)C_2H_4P(S)Ph_2$, $Ph_2P(S)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$,

respectively.

An attempt was made to sublime out the monosulphide from this mixture, but after heating at temperatures between 170 °C and 185 °C (under vacuum, 0.1 mm) for a few hours, the sublimed white solid was found to be mostly $Ph_2PC_2H_4PPh_2$, and the residue mostly $Ph_2P(S)C_2H_4P(S)Ph_2$. $Ph_2P(S)C_2H_4PPh_2$ could not, therefore, be prepared in a pure state due to its tendency to undergo disproportionation on heating.

N.m.r. tube experiments on mixtures of $Ph_2PCH_2PPh_2$ + $Ph_2P(S)CH_2P(S)Ph_2$, and $Ph_2PC_2H_4PPh_2$ + $Ph_2P(S)C_2H_4P(S)Ph_2$ in o-dichlorobenzene at 160 °C resulted in the quantitative production of $Ph_2P(S)CH_2PPh_2$ in the former, and the formation of a 1:2:1 mixture of $Ph_2P(S)C_2H_4P(S)Ph_2$, $Ph_2P(S)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ in the latter. Similar n.m.r. tube experiments on analogous mixtures of the corresponding phosphine selenides and phosphines revealed that $Ph_2P(Se)CH_2PPh_2$ was quantitatively produced within two minutes (at most) of dissolution, and that a 1:2:1 mixture of $Ph_2P(Se)C_2H_4P(Se)Ph_2$, $Ph_2P(Se)C_2H_4PPh_2$, and $Ph_2PC_2H_4PPh_2$ was produced within the same time interval.

Attempted preparation of $Ph_2P(Se)CH_2P(S)Ph_2$

$Ph_2P(S)CH_2PPh_2$ + selenium.

$Ph_2P(S)CH_2PPh_2$ (0.8 g, 1.92 mmol) was dissolved in benzene (25 ml) in a three-necked r.b. flask which had been flushed out with dry nitrogen. Selenium powder (0.16 g, 2 mmol) was added and the mixture was refluxed for 19 h. The reaction mixture was filtered hot and the filtrate allowed to cool. A white, crystalline solid separated out, the ^1H n.m.r. of which indicated that it was a mixture of $Ph_2P(Se)CH_2P(S)Ph_2$ plus $Ph_2P(S)CH_2P(S)Ph_2$ (ca. 3:1), with a trace of unreacted $Ph_2P(S)CH_2PPh_2$.

N.m.r. tube reactions.

$Ph_2P(S)CH_2PPh_2$ (66.6 mg, 0.16 mmol) and selenium (12.7 mg, 0.16 mmol) were mixed together in a n.m.r. tube in $CDCl_3$ (0.3 ml). The progress of the room temperature reaction was monitored periodically by n.m.r. spectrometry. After four days, $Ph_2P(Se)CH_2P(S)Ph_2$ was the sole product.

A similar mixture of $Ph_2P(S)CH_2PPh_2$ and selenium was heated at 155 °C for 22 h in o-dichlorobenzene, and again $Ph_2P(Se)CH_2P(S)Ph_2$ was produced, but an appreciable amount of $Ph_2P(S)CH_2P(S)Ph_2$ was also produced (relatively more, with respect to the amount of $Ph_2P(Se)CH_2P(S)Ph_2$, than was found in the benzene reflux preparation).

$Ph_2P(Se)CH_2PPh_2$ + sulphur

N.m.r. tube reaction

$Ph_2P(Se)CH_2P(Se)Ph_2$ (43.4 mg, 0.08 mmol) and $Ph_2PCH_2PPh_2$ (30.7 mg, 0.08 mmol) were dissolved in $CDCl_3$ in a n.m.r. tube, and a n.m.r. spectrum showed the quantitative production of $Ph_2P(Se)CH_2PPh_2$ (0.16 mmol). Sulphur (5.12 mg, 0.16 mmol) was added and, within five minutes, signals due to the methylene protons of $Ph_2P(Se)CH_2P(Se)Ph_2$, $Ph_2P(Se)CH_2P(S)Ph_2$, $Ph_2P(S)CH_2P(S)Ph_2$, $Ph_2P(Se)CH_2PPh_2$, and $Ph_2P(S)CH_2PPh_2$ were all detected. The n.m.r. of the final mixture (obtained after ca. 24 h at room temperature) exhibited three overlapping triplets in the ratio 1:2:1 arising from a 1:2:1 mixture of $Ph_2P(Se)CH_2P(Se)Ph_2$, $Ph_2P(Se)CH_2P(S)Ph_2$, and $Ph_2P(S)CH_2P(S)Ph_2$, respectively. The same product mixture was obtained when the reaction was carried out in deuteriobenzene.

N.m.r. tube reaction between $Ph_2P(Se)CH_2P(Se)Ph_2$ and $Ph_2P(S)CH_2PPh_2$

$Ph_2P(Se)CH_2P(Se)Ph_2$ (86.7 mg, 0.16 mmol) and $Ph_2P(S)CH_2PPh_2$ (66.6 mg, 0.16 mmol) were dissolved in $CDCl_3$ in a n.m.r. tube. After twenty

minutes, signals due to $Ph_2P(Se)CH_2P(S)Ph_2$ and $Ph_2P(Se)CH_2PPh_2$ were detected, which were twice the strength of the signals due to the two reactants. A further n.m.r. run after 22 h showed no change, the equilibrium state having been reached within the first twenty minutes.

CHAPTER 4

TERTIARY PHOSPHINE AND ARSINE CHALCOGENIDES AS INCLUSION COMPOUNDS

INTRODUCTION.

Tertiary Phosphine and Arsine Chalcogenides as Inclusion Compounds.

An inclusion compound consists primarily of two molecular species, one of which provides space in its structure in which molecules of the other are accommodated. These two species are known as the "host" which forms the essential structure, and the "guest" which is included, or contained in this structure. A specific host will form an inclusion compound with different molecules provided their dimensions satisfy the geometrical restrictions imposed by the available spaces in the structure. The interaction between host and guest is generally quite weak, the bonds being of the van der Waals type.

There are three categories into which inclusion compounds are classified, and these are based on the geometrical form of the space in which the guest molecules are located. Firstly, the clathrate or cage structure[105] is one in which one or more guest molecules are completely enclosed by host molecules. Monoammine-nickel (II) cyanide, $Ni(CN)_2NH_3$, forms clathrates with molecules of the general size and shape of benzene[106]. The nickel atoms and cyanide groups are arranged in single layers and above and below each of these are located the ammonia groups. A guest molecule is surrounded by an upper and lower layer of nickel cyanide, and by ammonia on the sides.

The second category is based on a channel structure[107] composed of open-ended channels which contain the guest molecules. Only the cross-sectional dimension of a molecule is critical for it to be a guest, and this is set by the smallest constriction that occurs in the channel space. Channel inclusion compounds whose host component is permanent, that is the host structure exists even in the absence of guest molecules, are generally prepared and decomposed without disturbing the host structure. Guest mole-

-cules diffuse into the solid host material from a solution or from the gas state. Molecular sieves[108] are just such host materials which are extensively used for purification and separation. They are produced synthetically and are related to the zeolite minerals. They are obtained in a variety of structures, each of which has characteristic channels which include molecules whose cross-sectional dimensions are below a certain magnitude. Because the channels extend indefinitely throughout the crystal, there is no restriction on the length of the guest molecule.

Channel compounds whose host structure requires guest molecules for stability are formed by crystallisation from a solution of host and guest molecules. Urea, for example, forms channel inclusion compounds with straight-chain hydrocarbons[107], whereas, although the urea crystals alone have a fairly open structure, the molecules are still too closely packed for a channel or other available free space in which guest molecules may be enclosed. In the urea-hydrocarbon adduct there are three interpenetrating spirals of urea molecules hydrogen-bonded together to form the walls of the hexagonal channel lattice in the unit cell. X-ray investigations have shown that the urea molecules form a hollow channel just large enough to accommodate the planar zig-zag hydrocarbon molecule. Extractive crystallisation with urea provides a practical means for selectively separating the straight-chain hydrocarbon components of petroleum fractions.

The third category of inclusion compounds are those of the layer type[109]. Here, the molecules or atoms of the host are arranged in layers between which guest molecules may be accommodated. Layer structures are fairly flexible and there is generally a wide variety of different molecules of various sizes and shapes that can be accommodated in a given layer structure. In fact, the included molecule partially determines the interlayer

distance. This effect should be compared with the fact that clathrate and channel structures are relatively inflexible, and are, therefore, much more selective in regard to size and shape of guest molecules than are the layer host compounds.

The host structure of some inclusion compounds exists only with an appropriate guest component. Otherwise, the unassociated solid host molecules assume a different structure. This is an important consideration in the equilibria, thermodynamics and methods of formation of inclusion compounds.

According to these considerations the use of inclusion compound formation as a means for the separation of a constituent from a mixture is obvious. If the molecules to be separated have the proper geometry and size to form an inclusion compound with a suitable host material, and there are no other molecules in the mixture that may also form an inclusion compound, a pure product is readily obtainable. Inclusion compounds are generally easy to form, by such means as absorption and crystallization, without the use of extreme temperatures. It is also easy to decompose an inclusion compound and to separate the host and guest because of the weak interaction between the two and considerable differences in their physical and chemical properties. This final stage in purification utilises simple thermal and solution methods, taking advantage of the guest being more volatile than the host or having a different solubility in a specific solvent.

In the field of separations and purification, clathrate chemistry has been neglected in the past. This may be attributed, at least in part, to the lack of development of adequate analytical techniques. With the improvement in methods available for structural analysis, particularly in X-ray crystallography, and this tool being available in many research es-

-tablishments, the science of clathrate chemistry has made rapid advances in recent years. Details of cavity type and dimensions as well as the types of bonding holding the host molecules together are derived from this powerful method. Once a particular clathrate series with one host and a series of guests has been established, crystal structure determinations for the clathrate and a knowledge of molecular dimensions of new guests under consideration can lead to good predictions of which guests will or will not be accommodated. Also by making subtle changes in the structure of the parent host molecule it is possible to produce quite marked changes in cavity geometry and guest selectivity. In fact, a systematic study of the structural modification of a particular host molecule was instigated in 1969 by MacNicol and co-workers[110], who first synthesized the thia-analogue of Dianin's compound, which appeared to be the earliest example of the deliberate preparation of a versatile organic clathrate host. They went even further by reporting a new approach[111] which has lead to the synthesis of inclusion hosts not directly related to any known host. They expressed the hope that in the not too distant future, in the light of crystallographic studies, it may be possible to tailor-make systems for specific inclusion or separation purposes.[111,112]

The Industrial Separation of the Xylene Isomers.

The xylenes and ethylbenzene are the aromatic C_8 fraction emerging from the cracking/platforming operations. The term "xylenes" generally applies to a mixture of any two or three of the dimethylbenzene isomers, i.e. ortho-, meta-, and para-xylenes. Many of the properties of the individual C_8 isomers are very similar. A consequence of this is that the production of individual components of very high purity becomes difficult. Since there is a great demand especially for pure para-xylene, much effort has been directed to accomplish these separations.

While o-xylene can be separated readily from m-xylene by distillation, it is only with difficulty that ethylbenzene can be distilled from p-xylene in pure form. It is not commercially possible to separate p-xylene from m-xylene by distillation. These two isomers may be separated by crystallization, since they form a eutectic mixture (with m.p.-53 °C) containing 87% of m-and 13% of p-xylene, resulting in the production of 99.5% pure p-xylene[113]. The extent of recovery of the pure isomer, however, is limited because of the eutectic formation. The addition of carbon tetrachloride to the xylenes feed mixture has been found to increase the p-xylene recovery from a nominal 60% to about 85% of that present in the feed, since p-xylene forms a 1:1 compound with CCl_4 (freezing point, 24.8 °C), whereas the ortho- and meta- isomers do not.[114]

The xylene isomers have been shown to form inclusion compounds. Schaeffer and co-workers[115] have reported that metal salt complexes of substituted pyridines (Werner complexes) are a class of clathrate hosts that are effective in separating aromatic isomers including the xylenes. The selectivity of these host compounds is based on the shape and size of the guest isomer. A specific example of such a host compound is tetra- (4-methylpyridine)nickel dithiocyanate. A one-stage separation from a feedstock mixture of the xylenes and ethylbenzene using this particular host resulted in the production of 64% pure p-xylene (Table 12).

Table 12

Isomer	Feedstock Mixture (%)	Separated Mixture (%)
p-xylene	19.3	64.0
o-xylene	19.1	5.1
m-xylene	50.6	13.7
ethylbenzene	11.0	17.2

If a three-stage process was used, it was estimated that a 97% pure p-xylene product would be obtained.[115]

It was reported that hosts of the Werner type involving any of the metal ions, Mn^{2+}, Fe^{2+}, Co^{2+}, or Ni^{2+}, were selective for p-xylene. Changes in the other components of the host, however, had a marked effect on the selectivity (Table 13).[116]

Table 13. Host Selectivity of Aromatic Isomers.

Host Compound	Preferred Guest
Ni(4-methylpyridine)$_4$(SCN)$_2$	p-xylene
Ni(4-ethylpyridine)$_4$(CNO)$_2$	o-xylene
Ni(3-ethyl-4-methylpyridine)$_4$(SCN)$_2$	m-xylene
Ni(4-acetylpyridine)$_4$(SCN)$_2$	ethylbenzene

De Radzitsky and Hanotier[117] also reported a number of these Werner complexes as hosts for C_8 isomers. In this instance, substituted primary benzylamines were complexed with nickel thiocyanate. They concluded that isomer separation could be carried out cyclically, and more effectively than by distillation, and claimed that the capacities of the hosts for the isomer were greater than could be achieved in adsorption.

Application of the adsorption technique to the separation of the xylene isomers, in particular the para and meta isomers, has been reported by Eberly et al.,[118] and Fleck et al.,[119] who both disclosed that a 10-13 Å molecular sieve could be used as the adsorbent in a vapour-phase process. This zeolite had pores of adequate size to admit all components of the xylene mixture, and, therefore, the separation was related to the heats of adsorption of the key components. As a consequence, such a separation required a number of stages to give relatively pure products. The development of an improved adsorbent that can remove p-xylene in high purity from the other C_8 aromatic isomers has been reported.[120] This was employed in

the Parex Process, licensed by Universal Oil Products, for the selective recovery of p-xylene. It was operated in the liquid phase at 120-180 °C, at moderate pressures, with a bed of molecular sieve zeolites as adsorbent. The recovery of the p-xylene was 99.7% and its purity 99.3% (with an adsorbent life greater than three years).

Allcock has described the unusual clathration behaviour of cyclotriphosphazenes,[121] and, for example, a process has been claimed for the separation of the xylene isomers. The efficiency of the process was illustrated by the preparation of 96% pure m-xylene in one step from a 25% p-xylene, 25% ethylbenzene, 50% m-xylene mixture.[122]

Of the three xylenes, the para-isomer has been the one for which demand has risen fastest. It is used as a starting material for terephthalic acid, p-$(HOOC)_2C_6H_4$, which is the basis for polyester fibres (e.g. 'Terylene').

The major use for o-xylene has been as a starting material for the manufacture of phthalic anhydride, which is used, in the form of a diester, as a plasticizer for poly(vinyl)chloride.

Ethylbenzene is primarily employed as a raw material for the manufacture of styrene, while m-xylene finds its principal outlet as its corresponding dibasic acid, isophthalic acid, although the amount of m-xylene so used is much less than either the ortho- or the para-isomer.

RESULTS AND DISCUSSION

The synthesis of the known compound,[69] 1,2-bis(diphenylphosphinoselenoyl)ethane, $Ph_2P(Se)C_2H_4P(Se)Ph_2$ (Host VI), (required for certain aspects of the work described in Chapters 1 and 3 of this thesis) from the corresponding diphosphine and two equivalents of elemental selenium, led to the interesting discovery that Host VI forms stable inclusion compounds when crystallized from various pure solvents (Table 14).

The crude solid product from the synthesis was recrystallised from benzene and dried by pumping on the vacuum line for 1 h. Microanalysis of the solid revealed, however, a rather high C and H content, and when further analysed by ^1H n.m.r. spectrometry, a sharp singlet due to the six equivalent protons of benzene was observed upfield from the aromatic protons of (VI). The solid was therefore pumped on the vacuum line for a further 2 h at room temperature, then at 80 °C for 3 h. Microanalysis of this solid indicated that the benzene had been removed leaving pure Host VI.

Recrystallisation of (VI) from cyclohexane was next attempted, since, it was thought, that if this molecule could be included, it would prove that the benzene was not simply solvent of recrystallisation but was indeed enclosed in some manner within the crystal structure of the host molecule. The recrystallised sample was dried under vacuum at room temperature for 2 h, then analysed by ^1H n.m.r. spectrometry which indicated a 4:1 ratio of host to guest molecules (Table 14). Subsequent recrystallisations from cyclohexane, however, did not always succeed in producing an inclusion compound, and when successful variable host to guest ratios were obtained.

Host VI shows remarkable guest selectivity when crystallised from certain solvent mixtures. Recrystallisation of this host from an equi-

Table 14 Inclusion Compounds of $Ph_2P(Se)C_2H_4P(Se)Ph_2$.

Guest molecule	Mole ratio of host:guest	Conditions for guest release
Benzene	0.75:1[a]	slow loss at room temperaure
Cyclohexane	4:1[c]	b
Toluene	2.4:1[c]	70 °C/0.04 mm
o-Xylene	0.8:1[c]	slow loss at room temperature
Naphthalene	2.5:1[a]	160 °C/0.08 mm
p-Xylene	2.9:1[a,c]	155 °C/0.08 mm
p-Chlorotoluene	3.0:1[a,c]	135 °C/0.08 mm
p-Dichlorobenzene	3.0:1[a]	145 °C/0.08 mm
p-Dibromobenzene	2.9:1[a]	170 °C/0.08 mm
sym-Tetrachloroethane	1.9:1[c]	100 °C/0.08 mm

[a] By gravimetric analysis. [b] Not determined. [c] By multiple ^1H n.m.r. integration. (See experimental section for a description of the determination of the mole ratios of host:guest).

-molar mixture of o-xylene, m-xylene, p-xylene, and ethylbenzene led to the recovery of host material containing 97.5% p-xylene, 0.6% m-xylene, 0.4% o-xylene and 1.5% ethylbenzene (analysed as described in the experimental section by quantitative i.r. spectrometry after liberating the guest molecules by vacuum sublimation at 160 °C). The use of a co-solvent (e.g. sym-tetrachloroethane) to increase the solubility of the host has enabled the removal of 33% of the p-xylene from such a mixture at a single crystallisation. Moreover, a similarly high selectivity for the para-isomer is retained for solvent mixtures of these components containing as little as 4% of that isomer.

The preference shown by Host VI for para-xylene may be general for para-disubstituted mononuclear aromatics of similar size. Thus, recrystallisation of this host from equimolar mixtures of ortho-, meta-, and para-chlorotoluenes produced an adduct containing 98.3% para-chlorotoluene, and recrystallisation from a similar isomer mixture of dichlorobenzenes led to an inclusion compound containing 94.8% of para-dichlorobenzene. The host-guest ratio for the adducts containing these para-isomers is nearly always ca. 3:1, whereas adducts with other guests show a more variable ratio (Table 14).

A potential host may have several crystal forms available to it, some of which will be unable to accommodate a solvent molecule because the cavity has the wrong shape or size. We have found, in general, that if crystal growth of Host VI (and related host molecules) commences above a certain temperature in a specific solvent (e.g. the critical temperature for Host VI when recrystallised from the xylenes is ca. 100 °C) or if the host comes out of solution too fast, then an empty crystal form results giving rise to the possibly erroneous conclusion that that particular solvent molecule cannot be included. The recrystallisation conditions can

be critical in determining whether a solvent molecule will be included or not. These conditions, therefore, require to be optimised, taking into consideration the host's concentration and solubility in the particular solvent under study. The rate of cooling after complete dissolution can also be critical and seeding with crystal fragments of the correct form, at the right temperature, is very often necessary to initiate the crystallisation of the inclusion compound (see Table 17A, p 135).

These practical considerations become even more important when the host compound is crystallized from solvent mixtures since the intention is to selectively remove as much as possible of one component of the mixture at a single recrystallisation. Any crystallisation of the "empty" crystal form can only reduce the efficiency of the separation process.

Simply stirring Host VI as a suspension in an equimolar mixture of the xylenes and ethylbenzene at room temperature for 20 h, however, resulted in the selective absorption of p-xylene into the crystal lattice of the host. A guest sample consisting of p-xylene (96.8%), m-xylene (0.7%), o-xylene (0.5%), and ethylbenzene (2.0%) was isolated from one such experiment. An absorption process would greatly simplify any commercial separative procedure utilising this host, since no dissolution of the host at elevated temperatures would be necessary and the slow cooling and seeding stage would not be required.

The ability of other molecules, structurally related to compound (VI), to exhibit significant inclusion behaviour has also been studied. The sulphur analogue of (VI), $Ph_2P(S)C_2H_4P(S)Ph_2$(VII), was found to be not nearly as versatile and exhibited minimal inclusion behaviour in comparison. Recrystallisation from p-xylene afforded an adduct with an approximately 6:1 host-guest ratio, but failed to include any guest when recrystallised from a 70:30 o-xylene/p-xylene mixture. Compound (VII)

also failed to show any tendency to absorb any of the C_8 isomers when stirred as a suspension in a solution consisting of a 1:1:1:1 mixture of the xylenes and ethylbenzene for 20 h at room temperature.

The compounds with three methylene groups between the phosphorus atoms, $Ph_2P(S)C_3H_6P(S)Ph_2$ (VIII) and $Ph_2P(Se)C_3H_6P(Se)Ph_2$ (IX), were found to be more versatile than (VII) but not as selective as (VI) when crystallised from solvent mixtures. Table 15 lists the inclusion compounds formed by (VIII) and (IX) when crystallized from certain pure solvents.

Compound (VIII) exhibited some selectivity when recrystallised from an equimolar mixture of the xylene isomers and ethylbenzene. Analysis of the guest by i.r. spectrometry indicated that this host was less selective than compound (VI), since the composition of the guest was p-xylene (58%), o-xylene (26%), m-xylene (13%), and ethylbenzene (3%). Also when recrystallised from a typical commercial feedstock mixture consisting of p-xylene (20%), o-xylene (15%), m-xylene (55%) and ethylbenzene (10%), ^1H n.m.r. analysis of the adduct indicated the increased presence of the meta-isomer at the expense of the para-isomer. No further selectivity tests on the xylenes and ethylbenzene were therefore undertaken due to the reduced selectivity of (VIII), which, in contrast to (VI), includes m-xylene when crystallized from this pure solvent (Table 15).

When recrystallised from a benzene-cyclohexane mixture, compound (VIII) formed a 2:1 host-guest adduct - the guest component of which consisted of approximately 80% cyclohexane and 20% benzene. Also when crystallised from a 3:1 p-xylene-benzene solvent mixture, the benzene component was preferentially included. An absorption test on a 1:1 mixture of ortho- and para-xylene confirmed the reduced selectivity of (VIII) found in the crystallisation experiments described earlier, both isomers being included although the amount of the para-isomer present was twice that of the ortho-isomer.

In contrast to compound (VIII), the original host molecule, (VI), failed to include p-diethylbenzene after repeated attempts to crystallise it from this pure solvent. This may indicate that the upper size limit for (VI) lies somewhere between p-dibromobenzene and p-diethylbenzene and may also explain the reduced selectivity of (VIII) when crystallised from the xylenes and ethylbenzene, since the cavity in the structure of host (VIII) must be significantly larger than that in host (VI) to accommodate a molecule of the size and shape of p-diethylbenzene. The smaller xylene isomers would therefore all be able to enter the cavity of host (VIII) and be included, although the para-isomer still would appear to be the best fit.

Host (IX), $Ph_2P(Se)C_3H_6P(Se)Ph_2$, in contrast failed to include any p-xylene after numerous attempts to recrystallise it both from the pure solvent and from an o-xylene/p-xylene mixture (80:20). Consequently, no further attempts were made to test the selectivity of this particular host molecule, although it may exhibit significant selectivity on a similar system to the xylenes; since, like the parent host (VI), it readily formed inclusion compounds with benzene and sym-tetrachloroethane (Table 15). Its increased solubility in cyclohexane also enabled the ready isolation of a 2:1 adduct with this solvent (Table 15).

The oxygen analogue of hosts (VIII) and (IX), $Ph_2P(O)C_3H_6P(O)Ph_2$, exhibited no inclusion behaviour when recrystallised from a 1:1 o-xylene/p-xylene mixture nor when stirred in a similar mixture for 18 h at room temperature. The compound appeared to be hygroscopic to some extent and the absorption of water may interfere with the process of clathration.

Thus, no other host molecule related to the parent host, $Ph_2P(Se)$-$C_2H_4P(Se)Ph_2$, has as yet been found to match the remarkable performance of this initially discovered clathrate host. Numerous other structural

Table 15 Inclusion compounds of $Ph_2P(S)C_3H_6P(S)Ph_2$ and $Ph_2P(Se)C_3H_6P(Se)Ph_2$.

Guest molecule	Mole ratio of host to guest for $Ph_2P(S)C_3H_6P(S)Ph_2$ [a]	Mole ratio of host to guest for $Ph_2P(Se)C_3H_6P(Se)Ph_2$ [a]
Benzene	2:1	1:1
Cyclohexane	2:1 [b]	2:1
p-Xylene	2:1	[c]
m-Xylene	2:1	[d]
p-Diethylbenzene	1:1	[d]
sym-Tetrachloroethane	[d]	1:1

[a] By multiple ^1H n.m.r. integration (see experimental section). [b] Crystallised from benzene-cyclohexane solvent mixture. Adduct contained ca. 80% cyclohexane and ca. 20% benzene (see text). [c] No p-xylene adduct could be formed with this host. [d] No attempt to produce this adduct was made.

modifications of the parent host can, however, be envisaged. The analogous compounds with four and more methylene groups between the phosphorus atoms seem likely candidates for investigation. Substitution of the aromatic rings attached to phosphorus may also allow fine adjustments to be made to the performance of the parent host and related compounds, and replacing the phosphorus atoms with arsenic atoms may result in the production of a further series of molecules which exhibit significant inclusion behaviour. In fact, one such compound, having been synthesized during the work described in Chapter 2 of this thesis, was briefly examined for indications of inclusion behaviour. Thus, $Ph_2As(S)C_2H_4As(S)Ph_2$, when recrystallised from benzene, was found to contain a small amount of included benzene which, like the benzene adduct of $Ph_2P(Se)C_2H_4P(Se)Ph_2$, appeared to be slowly released at room temperature, the crystals gradually changing from translucent to opaque. Recrystallisations from toluene, p-xylene, or cyclohexane, however, failed to produce any adducts, and an absorption test on a 1:1:1 mixture of the three xylene isomers did not result in the formation of an inclusion compound. Chatt and Mann[62] noted some time ago that a similar molecule, $PhBuAs(S)C_2H_4As(S)BuPh$, showed an unusually strong ability to separate from organic solutions with what they called solvent of recrystallisation. Thus, on recrystallisation from cyclohexane a 3:1 adduct was found to have been formed, which was unaffected by prolonged exposure in a vacuum at room temperature. When slowly heated, however, the cyclohexane was lost. Subsequently, Hinton and Mann[123] reported that certain cyclic tertiary phosphine sulphides also had a remarkable capacity for tenaciously retaining traces of solvent. Thus, triethylene diphosphine disulphide, $(S)P(CH_2CH_2)_3P(S)$, prepared from the corresponding diphosphine and sulphur in boiling benzene, had a host/guest composition of 8:1, after being heated at 125 ^{o}C/1 mm Hg for 4 h.

Application of clathration to isomer separation.

Four primary methods were generally employed for the preparation of inclusion compounds with a possible commercial application in mind: (1) dissolution of the host in the liquid feed mixture at elevated temperatures, then cooling, seeding, if desired, to precipitate the adduct, and filtering; (2) as in (1) but with the addition of a co-solvent to modify the host's solubility (the co-solvent should ideally not form an inclusion compound with the host); (3) stirring of the solid host as a suspension in the liquid feed mixture; and (4) contacting a suspension of the host with the feed mixture as in (3), but with the addition of an organic liquid (which did not dissolve the host nor enter into the process of clathration). Each of these could be operated successfully, and could conceivably be applied in a commercial process. Absorption of the guest from the vapour phase was also envisaged as being attractive, but could not be demonstrated due to the lack of suitable apparatus in which to carry out the process. Numerous attempts were made but at no time, with any of the different vessels used, was it possible to ensure that the guest did not condense on to the host rather than be absorbed from the vapour phase.

For absorption experiments, best results were usually obtained when the host compound was conditioned prior to use by formation of an adduct with the guest hydrocarbon to be separated from the mixture, followed by removal of the guest hydrocarbon. In the conditioning step the adduct was conveniently formed by crystallisation from solution.

Recovery of the guest was achieved, for example, by heating the adduct, if necessary at reduced pressure or, after separation of the adduct from the mixture, by dissolution of the adduct in a suitable solvent such as chloroform. If desired, the process may be applied to the removal of an unwanted component of a solvent mixture.

This process is of potential value with regard to the separation of isomers of the following compounds from one another, and also from other compounds: xylenes, chlorotoluenes, dichlorobenzenes, ethyltoluenes, cymenes, diethylbenzenes, toluidines, nitrotoluenes, methylanisoles and cresols.

Although a few other clathrate hosts exhibiting a preference for para-isomers have been described,[115-117] and have been used in the commercial separation of xylenes, to our knowledge none of these approaches the degree of selectivity or versatility afforded by $Ph_2P(Se)C_2H_4P(Se)Ph_2$.

Consultations with two major chemical companies gave the impression, however, that this host compound would probably be too expensive to make on a large tonnage scale, and that it would be difficult to meet satisfactory product quality in a single stage. The Parex Process, for example, which utilises a molecular sieve type adsorbent and is commercially easily operable, produces 99.2% pure p-xylene in a single stage with an adsorbent life greater than three years.

Therefore, although the process of clathration is technically very interesting and would appear to have commercial potential, it may not be competitive with other proven processes for para-xylene recovery. This series of clathrate hosts may, however, be applied to separation problems encountered in the smaller tonnage fine chemicals industry. For example, at present attempts are being made to adapt a host compound from this series with regard to the separation of the ethylcresol isomers. The N.R.D.C. have shown sufficient interest in the performance of these host compounds to take out on our behalf full patent coverage in four major countries.

A crystal structure analysis of the clathrate formed between Ph_2P-

-$(Se)C_2H_4P(Se)Ph_2$ and p-xylene is being undertaken, and this should provide details of the type of cavity and its dimensions. This might enable the host molecule to be tailored in such a way to improve the selectivity and general appeal of the compound as a means for the separation of organic compounds from mixtures by clathration.

Experimental

The spectroscopic instrumentation used was as described in the experimental section of Chapter 1. The ditertiary phosphines used in this work were obtained commercially from Strem Chemicals Inc., Fluorochem Ltd., or the Maybridge Chemical Company. The white crystalline ditertiary phosphine sulphides or selenides were prepared by the reaction of their respective diphosphines with a small excess of sulphur or selenium in refluxing benzene solution. The diphosphine dioxide, $Ph_2P(O)C_3H_6P(O)Ph_2$, was prepared from the diphosphine and two moles of hydrogen peroxide (27½% solution) in refluxing acetone. The various solvents were all commercially available.

The following three examples illustrate the methods used to prepare inclusion compounds of the clathrate host $Ph_2P(Se)C_2H_4P(Se)Ph_2$ (Host VI) from equimolar mixtures of the xylenes and ethylbenzene:

Example 1 (No co-solvent)

3 g of $Ph_2P(Se)C_2H_4P(Se)Ph_2$ (Host VI) was dissolved in 25 ml of an equimolar mixture of o-xylene, m-xylene, p-xylene and ethylbenzene at 383 K. The solution was allowed to cool at approximately 0.5-1.0 °/min. Seeding with crystal fragments which contained included p-xylene initiated crystallisation when the temperature was 360 K. 2.9 g of adduct (VI)-p-xylene was isolated. The adduct was purified by decantation then evacuation at room temperature.

The separated hydrocarbon was recovered from the adduct by heating the adduct at reduced pressure. The isolated hydrocarbon was analysed by quantitative i.r. spectrometry and shown to consist of 95.5% p-xylene, 2.5% ethylbenzene, 1.2% m-xylene and 0.8% o-xylene (all values subject to an error of ± 0.1%).

Example 2 (with $CHCl_3$ as co-solvent)

2 g of Host VI was dissolved in 25 ml of an equimolar mixture of o-xylene, m-xylene, p-xylene, ethylbenzene and chloroform at 363 K. This solution was allowed to cool at approximately 0.5-1.0 °/min. No seeding was employed. 1.9 g of adduct (VI)-p-xylene was isolated. This was purified by decantation and evacuation at room temperature to remove surface liquid.

The separated hydrocarbon was recovered from the clathrate inclusion compound as in Example 1. Analysis by ^1H n.m.r. spectroscopy indicated that the separated hydrocarbon consisted of p-xylene (95% or better) with trace quantities only of ethylbenzene, o-xylene, or m-xylene.

Example 3 (Absorption Method)

1.90 g of Host VI was stirred for 20 h under a nitrogen atmosphere in 8 ml of an equimolar mixture of o-xylene, m-xylene, p-xylene and ethylbenzene at 295 K. 1.85 g of adduct (VI)-p-xylene was isolated after filtration, n-pentane washing, and evacuation at room temperature.

The separated hydrocarbon was again recovered from the adduct by heating the adduct at reduced pressure. The isolated hydrocarbon was analysed by quantitative i.r. spectrometry and shown to consist of 96.8% p-xylene, 2.0% ethylbenzene, 0.7% m-xylene, and 0.5% o-xylene (all values subject to an error of $\pm$ 0.1%).

Determination of mole ratio of host to guest

(a) By gravimetric analysis

A small amount of the adduct (ca. 30-50 mg) was placed in a weighed 50 ml r.b. flask and then weighed again to determine the exact amount of adduct used. The flask was then attached to the vacuum line and evacuated. It was immersed in an oil-bath and heated to a temperature slightly above the temperature for guest release determined prior to analysis. The

solid adduct was observed to "jump" on release of the guest. Heating was maintained until no further signs of guest loss were evident. The flask was then carefully reweighed to determine the weight loss and consequently the mole ratio of host to guest. This method was conveniently and easily applied although some difficulty was experienced in preventing the balance from slipping at the fourth decimal place. The results obtained by this method are listed in Table 14 (Discussion Section).

(b) By multiple ^{1}H n.m.r. integration

The adduct could be readily analysed for host:guest mole ratio by integration of the area under the signal due to the methylene protons of the host molecule relative to that under the signals of certain guest molecules which contained protons well separated from other signals in the ^{1}H n.m.r. spectrum of the adduct dissolved in deuteriochloroform. This method was generally applied more than the gravimetric method since a result of similar accuracy could be rapidly determined simply by running the ^{1}H n.m.r. spectrum of the dissolved adduct. In fact, a qualitative means for determining whether or not an adduct had been formed between $Ph_2P(Se)C_2H_4P(Se)Ph_2$ in particular and a potential guest molecule was to observe whether the crystalline adduct fragments remained on the bottom of the n.m.r. tube on addition of $CDCl_3$ or whether they rose and floated at the surface of the solution prior to complete dissolution. The crystals which were less dense than $CDCl_3$ generally contained included guest, the denser form was always empty. Only when the guest molecule was too big to be contained within the open structure of the less dense form would a negative result be obtained from a Host VI adduct which was less dense than $CDCl_3$.

The values obtained from this method for determining host:guest ratios are listed in Tables 14 and 15 (Discussion Section). Table 16 lists selected n.m.r. characteristics of the various hosts and several

Table 16 Selected host and guest n.m.r. characteristics.

Host or Guest Molecule	N.m.r. characteristics[a]
$Ph_2P(Se)C_2H_4P(Se)Ph_2$	CH_2, 2.87 (d, $J \cong 2$ Hz)
para-Xylene	Ph, 7.10 (s); CH_3, 2.30 (s)
para-Chlorotoluene	CH_3, 2.35 (s)
sym-Tetrachloroethane	CH, 5.95 (s)
Toluene	CH_3, 2.37 (s)
Cyclohexane	CH_2, 1.40 (s)
ortho-Xylene	Ph, 7.15 (s); CH_3, 2.25 (s)
$Ph_2P(S)C_2H_4P(S)Ph_2$	CH_2, 2.73 (d, $J \cong 2$ Hz)
$Ph_2P(S)C_3H_6P(S)Ph_2$	CH_2, 1.6-3.0 (m)
meta-Xylene	Ph, 7.0 (s)[b]; CH_3, 2.30 (s)
benzene	C_6H_6, 7.35 (s)
para-Diethylbenzene	Ph, 7.15 (s); CH_2, 2.63 (q); CH_3-1.20 (t)
$Ph_2P(Se)C_3H_6P(Se)Ph_2$	CH_2, 1.7-3.1 (m)

[a] In $CDCl_3$. Proton chemical shifts (δ/p.p.m.) relative to internal T.M.S. (s)=singlet, (d)=doublet, (t)=triplet, (q)=quartet, and (m)=multiplet. [b] Major aromatic signal; minor signals also observed slightly downfield.

of the guests with easily assignable proton resonances. Numerous recrystallisations of Host VI from solvent mixtures of varying amounts of the xylene isomers and ethylbenzene (with or without added co-solvent) were carried out during the course of this investigation to determine the limitations to this host's ability to selectively remove one component from such a mixture. The optimum recrystallisation conditions necessary for the growth of the correct crystal form and the various factors which tended to favour (or disfavour) the crystallisation of the inclusion compound were thus discovered. Some of these recrystallisation conditions are presented in Table 17A. Similarly, Table 17B lists the experimental conditions employed when an inclusion compound was formed by absorption of the guest into the solid host's structure.

Quantitative analysis of included guest by i.r. spectrometry.

Included guest was usually recovered from the separated and dried crystalline adduct by heating the adduct under vacuum at a temperature sufficient to cause guest release. The guest was isolated by trapping it at 77 K, then analysed quantitatively by a conveniently and easily applied i.r. absorption method. Standard mixtures of, for example, the xylene isomers and ethylbenzene were prepared consisting of small percentages (0-3%) of the ortho- and meta-xylenes and ethylbenzene in para-xylene (ca. 95%). Each of these four C_8 isomers exhibited a characteristic aromatic C-H stretching band in the region 690-800 cm^{-1} (p-xylene, 797; m-xylene, 771; o-xylene, 744; and ethylbenzene, 698 cm^{-1}). By plotting the optical density (O.D.) against the % composition of each standard mixture, straight line graphs could be drawn for each isomer. A guest sample was then analysed simply by measuring the difference in O.D. between pure p-xylene (as the base line) and each of the bands due to the "impurities" in the largely p-xylene-containing guest sample. The percentages of these three components present in the guest sample could then

Table 17A. Selectivity behaviour of $Ph_2P(Se)C_2H_4P(Se)Ph_2$ towards the xylene isomers and ethylbenzene (RECRYSTALLISATION)

C_8 SOLVENT MIXTURE (%)				RECRYSTALLISATION CONDITIONS					
p-Xylene	m-Xylene	o-Xylene	Ethyl-benzene	Concen-tration (g/l)	p-Xylene included?	Estimate of cooling rate [a]	Seeding em-ployed ? (Temp/°C)	Stirring as solution cooled ?	Temperature crystals first observed (°C)
50	-	50	-	16	YES	FAST	NO	NO	100
30	-	70	-	16	YES	FAST	NO	NO	100
25	25	25	25	16	YES	FAST	NO	NO	100
25	25	25	25	67	YES	SLOW	YES (86)	NO	74
25	25	25	25	100	NO	SLOW	NO	NO	ca. 100
25	25	25	25	120	YES[b]	SLOW	YES (86)	NO	100
25	25	25	25	150	YES[b]	SLOW	NO	YES	100
20	-	80	-	16	YES	FAST	NO	NO	100
20	40	20	20	146	NO	SLOW	NO	YES	100
20	40	20	20	40	YES	FAST	NO	NO	100
20	20	20	20	80[c]	YES[b]	SLOW	NO	NO	100
9	18	9	9	546[d]	YES[b,f]	SLOW	YES (80)	NO	100
8	17	8	8	500[e]	NO[f]	SLOW	YES(100)	NO	100
8	55	25	12	500	NO	SLOW	NO	NO	100
8	55	25	12	80	NO	FAST	YES(105)	NO	100
4	32	32	32	16	YES	FAST	NO	NO	100
4	32	32	32	16	NO	FAST	NO	NO	100
2	48	25	25	41	NO	FAST	YES (80)	YES	100

[a] A fast cooling rate was usually in excess of 1 °/min and involved allowing the solution to return to room temperature without any attempts to slow heat loss to the surroundings. A slow cooling rate was usually between 0.1 and 1.0 °/min, and involved allowing the solution to cool to room temperature gradually over a period of a few hours, e.g. by gradually reducing the temperature of the oil bath in which the solution was immersed. [b] p-Xylene included to a reduced extent (ca. 4:1 instead

Table 17A contd.

of 2.9:1). [c] Remainder (20%) of solvent mixture was a co-solvent, chloroform, which increases the solubility of the host in the guest mixture. [d] sym-Tetrachloroethane (55%) was the co-solvent. [e] sym-Tetrachloroethane (59%) as co-solvent. [f] sym-Tetrachloroethane was included instead of p-Xylene (Host/Guest ratio, 1.9:1). Illustrates the need for choosing a co-solvent which is not included by the host molecule.

Table 17B Selectivity behaviour of $Ph_2P(Se)C_2H_4P(Se)Ph_2$ towards the xylene isomers and ethylbenzene (ABSORPTION)

C_8 SOLVENT MIXTURE (%)				ABSORPTION CONDITIONS[a]			
p-Xylene	m-Xylene	o-Xylene	Ethylbenzene	Concentration (g/l)	p-Xylene included ?	STIRRING (h)	STANDING ONLY (h)
50	-	50	-	228	YES	YES (18)	-
25	25	25	25	231	YES	YES (20)	-
25	25	25	25	200	NO	-	YES (20)
25	25	25	25	246	NO	YES (1)	-
20	55	25	-	234	YES[b]	-	YES (20)
10	60	30	-	320	YES[b]	-	YES (18)
10	60	30	-	342	YES	YES (20)	-
8	55	25	12	232[c]	NO	-	YES (72)
2.5	15	7.5	-	300[c]	NO	YES (20)	-

[a] The solid host was either stirred or allowed to stand in a solution of the guest isomer mixture for a certain time at room temperature. [b] p-Xylene included to a lesser extent than normal (4.4:1 instead of 2.9:1). [c] Remainder (75%) of solvent mixture was n-pentane, in which the host is completely insoluble at room temperature.

be read off the graphs and thus the percentage purity of the p-xylene guest determined. The same procedure was followed for the determination of the percentage purity of the p-chlorotoluene obtained from a recrystallisation of Host VI from a 1:1:1 mixture of the chlorotoluenes. The method required to be adapted slightly for the dichlorobenzene isomers, however, since p-dichlorobenzene is a solid at room temperature. The guest sample was dissolved in the minimum volume of benzene (which has a band at 676 cm^{-1} and is clear between 750 and 830 cm^{-1} where the dichlorobenzenes absorb) and then analysed as described above for the xylenes. The error in the analysis method was estimated at $\pm$ 0.1%, whereas when the guest sample from the recrystallisation of the less selective Host VIII ($Ph_2P(S)C_3H_6P(S)Ph_2$) from a 1:1:1:1 mixture of the xylene isomers and ethylbenzene was analysed, the error was considered to be $\pm$ 1%. This was due to the increased amounts of the ortho- and meta- xylenes present in this guest sample, preventing any spectrometer expansion scale from displaying the bands due to the lesser components on the chart paper. Diluting the sample in p-xylene by a factor of 10 enabled an estimate of the percentage composition of the sample to be made, since standard solutions could be prepared closer and closer to the composition of the guest by varying the amount of each isomer until the difference between the standard and guest solutions was minimal. By plotting the O.D. of three standard mixtures close to the guest composition against the percentage of the three minor components in each standard, straight-line graphs could be drawn, allowing the amounts of the three isomers present in the largely p-xylene-containing guest sample to be read off the graphs.

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